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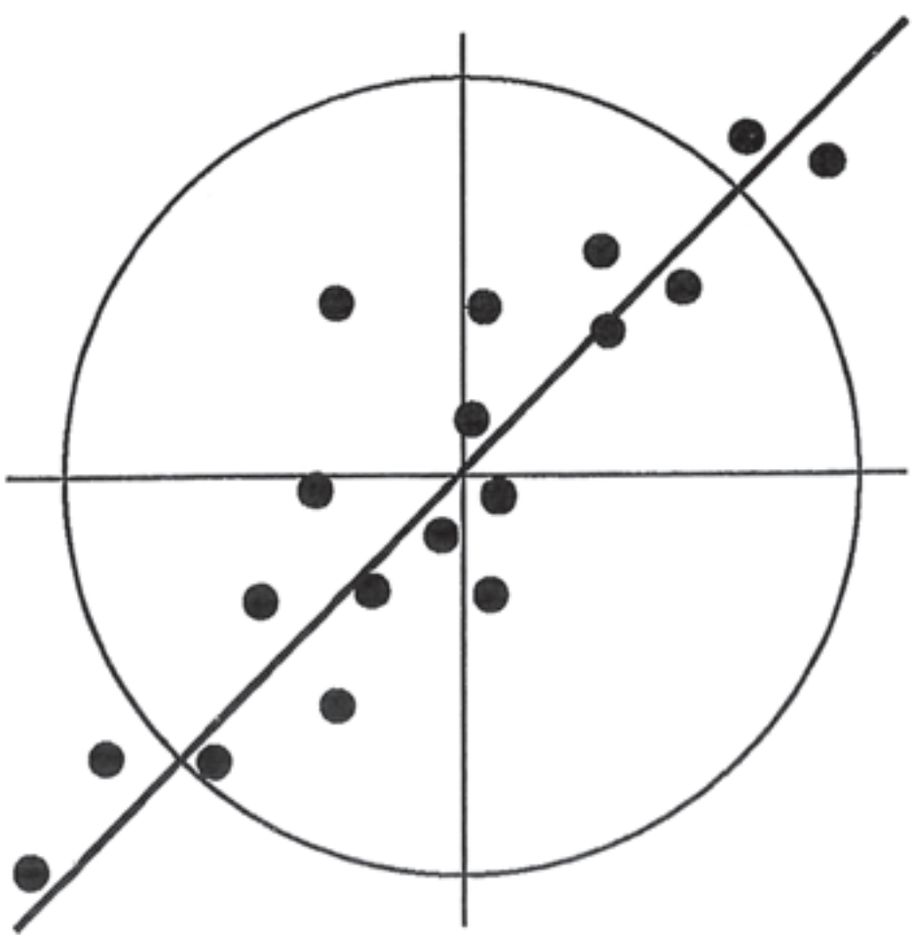
Intercomparison 1024: pH, Cond, HCO_3, NO_3-N, Cl, SO_4, Ca, Mg, Na, K, TOC, Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn



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REPORT

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Abstract

75 laboratories received samples for the intercomparison 1024, and 65 laboratories in 25 countries submitted results. Two sample sets were used, one for the determination of major ions, and one for heavy metals. Based on the general target accuracy of ± 20 %, 75 % of the overall results were considered as acceptable. The best results were reported for the analytical variables sodium, cadmium and manganese, with 93, 88 and 85 % acceptable results, respectively. Low percentage of acceptable results was observed for pH with only 49 % acceptable results, and copper with 51 % acceptable results. Harmonization of the analytical methods used, and the practical procedures followed, may probably be the most important way to improve the comparability for these parameters.

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CONVENTION ON LONG-RANGE
TRANSBOUNDARY AIR POLLUTION

INTERNATIONAL COOPERATIVE PROGRAMME ON
ASSESSMENT AND MONITORING OF ACIDIFICATION
OF RIVERS AND LAKES

Intercomparison 1024

pH, Cond, HCO_3, NO_3-N,
Cl, SO_4, Ca, Mg, Na, K, TOC,
Al, Fe, Mn, Cd, Pb, Cu, Ni, and Zn

Prepared by the ICP Waters Programme Centre
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Preface

The International Cooperative Programme on Assessment and Monitoring Effects of Air Pollution on Rivers and Lakes (ICP Waters) was established under the Executive Body of the UNECE Convention on Long-range Transboundary Air Pollution (LRTAP) in July 1985. Since then ICP Waters has been an important contributor to document the effects of implementing the Protocols under the Convention. Numerous assessments, workshops, reports and publications covering the effects of long-range transported air pollution has been published over the years.

The ICP Waters Programme Centre is hosted by Norwegian Institute for Water Research (NIVA), while the Climate and Pollution Agency (Klif) leads the programme. The Programme Centres work is supported financially by KLIF.

The Programme objective is to establish an international network of surface water monitoring sites and promote international harmonization of monitoring practices. One of the aims is to detect long-term trends in effects of acidic deposition on surface water chemistry and aquatic biota, and to reveal the dose/response relationship between water chemistry and aquatic biota.

One of the tools in this work is inter-laboratory quality assurance tests. The bias between analyses carried out by the individual participants of the Programme has to be clearly identified and controlled.

We here report the results from the 24th intercomparison of chemical analysis.

Oslo, September 2010

Håvard Hovind

Contents

Summary

Intercomparison 1024 was organized as a part of the between-laboratory quality control programme, as stated in "Manual for Chemical and Biological Monitoring" (1), by the International Cooperative Programme on Assessment and Monitoring of Acidification in Rivers and Lakes (ICP Waters).

The intercomparison was performed in July - August 2010, and included the determination of major ions and metals in natural water samples. The participants were asked to determine pH, conductivity, alkalinity, nitrate, chloride, sulphate, calcium, magnesium, sodium, potassium, total organic carbon, aluminium, iron, manganese, cadmium, lead, copper, nickel and zinc.

Two sample sets were prepared for this intercomparison, one for the determination of the major ions, and one for the heavy metals. 123 laboratories were invited to participate in this intercomparison, and the samples were sent to the 75 laboratories who accepted to participate. 65 laboratories submitted results to the Programme Centre before the final statistical treatment of the data. 25 countries were represented in this laboratory group (see Appendix A, page 41).

The median value of the results received from the participants for each variable was selected as "true" value. On average 75 % of the result pairs were considered as acceptable, the target limit being the median value ± 20 %, except for pH and conductivity where the special acceptance limits were selected, being ± 0,2 pH units and ± 10 %, respectively.

For pH, the accuracy limit was as in earlier intercomparisons extended from the target acceptance limit of ± 0,1 units to ± 0,2 units, and this time only 49 % of the result pairs were acceptable even using this special limit. This is not accptable, however, the number of acceptable results seems to be dependent on the samples used from year to year. A total error of ± 0,2 units for pH measurements is a more reasonable basis for the assessment of the accuracy between laboratories than the target limit of ± 0,1 units.

The best results were reported for the analytical variables sodium, cadmium, and manganese where 93, 88 and 85 % of the results, respectively, were acceptable. The worst results were observed for pH (49 %), and copper (51 %). The main reason for less acceptable results is probably the low concentrations in the samples used for some analytical variables. A reduced stability may explain the result for nitrate. The fact that some laboratories are using equipment which is not sensitive enough for the low concentrations used in this intercomparison.

More than 80 % acceptable results were obtained for the nine parameters conductivity, magnesium, sodium, potassium, total organic carbon, iron, manganese, cadmium and zinc, 70 - 79 % acceptable results were obtained for alkalinity, chloride, sulphate, calcium, aluminium and lead, 60 – 69 % for nickel, and 50 – 59 % for nitrate and copper.

1. Introduction

As stated in "Manual for Chemical and Biological Monitoring" (1), between-laboratory quality control is necessary in a multilaboratory programme to assure clear identification and control of the bias between analyses carried out by individual participants of the Programme. Such biases may arise by use of different analytical methods, errors in the laboratory calibration solutions, or through inadequate within-laboratory control.

The between-laboratory control carried out by the Programme Centre is based on the "round robin" concept and the procedure of Youden (2, 3), which is briefly described in Appendix C. This twentyfourth intercomparison test, called 1024, included the determination of the major components and metal ions in natural water samples: pH, conductivity, alkalinity, nitrate, chloride, sulphate, calcium, magnesium, sodium, potassium, total organic carbon, aluminium, iron, manganese, cadmium, lead, copper, nickel and zinc.

2. Accomplishment of the intercomparison

The preparation of the sample solutions is described in Appendix B. The results of the control analyses performed at the Programme Centre are also summarized in the same place. On the Task Force meeting in Burlington, Canada, in October 2009, it was decided that two sample sets as earlier should be included in this intercomparison, one sample pair for the determination of the major ions, and one for the heavy metals. It was decided that total organic carbon and aluminium should be included in this round also.

The samples were mailed from the Programme Centre on June 24th 2010, and the following day. Most of the participating laboratories received the samples within one week, with some few exceptions. It is important that the delivery address for the samples is correctly given, one set of samples were not delivered to the laboratory, but were returned to the organizer of this intercomparison.

To ensure that the effect of possible alterations in the solutions is minimized, the participants were asked to analyze the samples as soon as possible, and return the analytical results within one month after the samples arrived at the laboratory. By different reasons a few laboratories asked for some delay for reporting the results to the Programme Centre, which they were permitted to do. However, the results had to be reported before the statistical calculations. Most results were received within the middle of August, the last results included in the report were received at the end of the month. Nine laboratories who received samples did not return analytical results, and one box of samples were returned to the Programme Centre.

3. Results

123 laboratories were invited to participate in this ICP Waters intercomparison. 75 of the laboratories accepted and therefore samples were mailed to them, however, 74 laboratories received the samples. The 65 laboratories which submitted results to the Programme Centre, are representing 25 countries. Some laboratories submitted results a couple of weeks after the deadline, after a reminder letter was mailed to them. The last results were received at the end of August. A survey of the participants and their code numbers are listed in Appendix A, which also includes a table summarizing how many laboratories are participating from each country (see page 44).

The analytical results received from the laboratories were treated by the method of Youden (2, 3). A short description of this method, and the statistical treatment of the analytical data, is presented in Appendix C. The purpose of this test is to evaluate the comparability of the analytical results produced by the laboratories participating in the International Cooperative Programme. The real "true value" is not known exactly for the natural water samples used in this intercomparison. Therefore, we selected the median value, determined from the analytical results submitted by the participating laboratories after outliers were excluded, as the "true value" for each analytical variable. The median value is considered to be an acceptable estimate of the true value for this purpose, as long as most of the participants are using essentially the same analytical method. For certain variables, for instance pH, this may represent a problem as the different methods used may produce systematically different results (stirring, non-stirring, and equilibration of the test solution), and we cannot argue that one method is more correct than the others.

The results are illustrated in Figure 1 - 19, where each laboratory is represented by a small circle and an identification number. Some laboratories with strongly deviating results may be located outside the plot. The great circle in the figures are representing a selected accuracy limit, either the general target limit of ± 20 % of the mean true values for the sample pair, or a special accuracy limit as defined in the sections below. A summary of the results of intercomparison 1024 is presented in Table 1. The individual results of the participants are presented in Table 4 in Appendix D, sorted in order of increasing identification number. More extensive statistical informations are presented in the Tables 5.1 - 5.19 in Appendix D.

3.1 **pH**

The reported results for pH are graphically presented in Figure 1, where the radius of the circle is 0,2 pH units, and visualizes the degree of comparability between the pH results from the participating laboratories. The values reported by the laboratories are given in Table 5.1.

The participating laboratories determined pH in the test solutions using their own routine method. An electrometric method was used by all laboratories. 61 laboratories reported results for pH, 26 of the laboratories of this group indicated that they read the pH value during stirring the solution, while 34 read the pH value in a quiescent solution. The stirring are normally lowering the observed pH result. However, in this intercomparison the median values are not significantly different in the stirred samples compared to the non-stirred samples (see Table 1).

One laboratory equilibrated the solutions by bubbling with air containing 350 ppm CO_2 before reading the pH value. The reported results are systematically higher than the mean value of the other laboratories. The information obtained by pH measurement after equilibrating the solution, is different from pH-values read directly, or during stirring the sample. Especially in cases where the difference between the results produced by different methods are greater than here, it would be questionable to establish a "true value" based on the median value for all the reported results for pH. In such a case it should be discussed whether an individual "true value" for each method would be more appropriate. In the intercomparison 1024 we have used the median value of all the reportede results, after the outliers have been excluded. However, only 49 % of the results were acceptable, that is within the median value ± 0,2 pH units.

The control analyses carried out at the Program Centre covered the whole periode when the participants were analyzing their samples, and it was observed a small reduction in measured pH from the start to the end of the periode. However, the reduction was less than 0,2 pH units. We should also be aware of the possibility that the equilibrium of the samples may be influenced by variations in pressure and temperature when they are mailed by air to the participants.

Figure 1 is illustrating that the reported results are rather spread out along the 45 ° line, indicating that the results are influenced by systematic effects on the results. The systematically lowest pH results in Figure 1 are dominated by laboratories stirring the sample during reading the pH value. Some systematic deviations observed in Figure 1 may also be due to errors in the instrument, or more likely the electrodes, as different electrodes may give rise to different results (4, 5). The main reason for the differences in the reported results is probably connected to the small differences in the analytical methods used by the participants. Random errors are also affecting the results, and to a greater degree for pH than many other variables, illustrated in Figure 1 by the spread of the small circles away from the 45° line for many laboratories.

3.2 **Conductivity**

The conductivity results are presented in Figure 2, where the great circle is representing an accuracy limit of ± 10 %, which is only half of the target accuracy limit given in the Manual (1). The reported results are given in Table 5.2. Some laboratories obviously reported the conductivity results in another unit than the requested one, which should be mS/m at 25 °C, the reported results being at least one decade wrong. After questioning these laboratories about the unit used, some of them reported the unit they really used, and thus the results from these laboratories were recalculated to mS/m.

All participants used an electrometric method for the determination of conductivity. Most laboratories achieved very good agreement between the results for this variable. Figure 2 is showing that systematic errors are dominating the results, both in positive and negative directions. A proper temperature correction is necessary when determining this variable, as the conductivity is changing by about two percents pr. degree at room temperature. If the accuracy limit was extended to the target value of ± 20 %, defined in the Manual (1), 4 more results which is located outside the 10 % acceptance circle, would be located within the circle

and thus be defined as acceptable (then 90 % of the results would have been acceptable). An acceptance limit of ± 10 % seems to be a more reasonable demand.

3.3 **Alkalinity**

The alkalinity results are illustrated in Figure 3, and the reported results are given in Table 5.3. 45 laboratories reported results for alkalinity, and nearly one half of the participants used the Gran plot titration method which is the suggested reference method in the Manual (1). The others used end point titration, either to pH = 4,5 and 4,2, or to one certain pH value only (4,5, 5,4 or 5,6). The results reported for the method using titration to both pH = 4,5 and 4,2 were very close to the results produced with the Gran plot method.

The results for alkalinity are spread out along the 45 ° line, as illustrated in Figure 3, indicating that systematic effects are the dominating reason for the differences observed between many results. At the same time some random errors are contributing to the spreading out of some results from the 45 ° line. The laboratories using the Gran plot titration or titration to both pH 4,5 and 4,2, reported results located within the acceptance limits represented by the circle in figure 3. Some of the laboratories titrating to one end point only, have reported systematically lower results for both samples.

The alkalinity value may vary significantly with the end-point pH used for the titration. In waters containing high concentrations of total inorganic carbon, the equivalence point is close to pH = 5,4. In such a case, the relative error introduced by assuming a fixed end-point pH, is negligible. However, at lower alkalinities normally encountered in areas sensitive to acidification, the “total fixed end-point method” may overestimate the true alkalinity or the “equivalence” alkalinity. It is possible that this may be the explanation of the many deviating results in this intercomparison.

The overall result for alkalinity in this intercomparison is somewhat better compared to the last intercomparisons, 74 % of the results being acceptable.

3.4 **Nitrate + nitrite**

The results reported for this parameter are presented in Figure 4, and the reported values are given in Table 5.4. The circle in Figure 4 represents a general target accuracy of ± 20 %. Ion chromatography is used by about two third of the participants. The others are determining this analytical variable by photometric methods. Most of these laboratories are using an automated version of the cadmium reduction method. There is no significant difference between the results determined by these two methods. The hydrazine method was used by two laboratories, one with acceptable results. Three laboratories obviously reported the results in a wrong unit, and the results were corrected to µg/l after clarification with the laboratory.

In this intercomparison only 57 % of the results are evaluated as acceptable, which is comparable to the corresponding intercomparisons last year. However, this is not acceptable. The control analyses at the Programme Centre demonstrated that these samples were not very stable with respect to the content of nitrate and nitrite, a small reduction in the results were observed throughout the whole periode of the intercomparison. Also, some of the participants

indicated that the samples were less stable with respect to the nitrate content. During transport to the laboratories the samples may be affected by the environmental conditions. The spread of the results out from the 45 ° line may indicate that there are some contribution from random effects.

As nitrite is absent in the sample solutions used here, the results from the photometric and ion chromatographic methods should be directly comparable, as illustrated in Table 2.

3.5 **Chloride**

The chloride results are presented in Figure 5, and the reported results from the participants are given in Table 5.5. The target accuracy of ± 20 % is represented by the great circle in figure 5. 89 % of the laboratories determined chloride by ion chromatography. The greatest deviations are observed for the argentometric method, the results being systematically too low.

79 % of the result pairs in this intercomparison are acceptable.

3.6 **Sulphate**

The sulphate results are illustrated in Figure 6, and the reported values are given in Table 5.6. The circle is representing the target accuracy of ± 20 %. Ion chromatography is used by 89 % of the laboratories for determination of the sulphate content of the samples. One laboratory used a photometric method based on the dissociation of the barium-thorin complex, the results being systematically too low. Two laboratories used ICP-AES for the determination of total sulphur, and then recalculated the result to mg/l sulphate, the result being somewhat high.

73 % of the result pairs are acceptable this time, somewhat lower than earlier.

3.7 **Calcium**

The calcium results are illustrated in Figure 7, and the reported values are given in Table 5.7. The target accuracy is ± 20 %, and is represented by the great circle in Figure 7. 56 laboratories reported results for calcium, and only 11 of them used the traditional flame atomic absorption spectrometry for the determination. The ICP technique is used by 16 laboratories, and three of them used ICP-MS. An increasing part of the laboratories, this time 27, used ion chromatography. Two laboratories used a titrimetric method with EDTA for the determination of calcium, the precision of this method is less than for the other methods.

77 % acceptable result pairs is a good result.

3.8 **Magnesium**

The magnesium results are presented in Figure 8, and the reported values are given in Table 5.8. The analytical methods used by the participants are the same as for the determination of calcium. 11 laboratories are still using flame atomic absorption spectrometry for the

determination of magnesium. ICP atomic emission spectrometry was used by 16 laboratories, of which ICP-MS was used by three. 27 laboratories used ion chromatography. Systematic errors are dominating the results being outside the acceptance limit. This time, 82 % of the results are located inside the target accuracy of ± 20 %.

3.9 **Sodium**

The sodium results are presented in Figure 9, where the great circle is representing the general target accuracy of ± 20 %. The reported values are given in Table 5.9. 57 laboratories reported results for sodium, and only nine of these used flame atomic absorption spectrometry for the determination this time. ICP-AES was used by twelve laboratories and ICP-MS by three. However, in many laboratories the ion chromatographic technique becomes increasingly more popular in routine determination of the alkaline metals, 27 participants used ion chromatography in this intercomparison. Six laboratories used flame photometry. 93 % of the result pairs are located within the general target accuracy of ± 20 %, which is considered as a very good result.

3.10 **Potassium**

The potassium results are presented in Figure 10. The great circle is representing the target acceptance limit of ± 20 %. The reported values from 57 laboratories are given in Table 5.10. As for sodium, only ten laboratories used flame atomic absorption spectrometry for the determination of this element, and emission spectrometry is used by the same laboratories as for the determination of sodium. The deviations observed in Figure 10 are both of systematic and random nature. This time 82 % of the result pairs are considered acceptable, and this is better than in the last intercomparison.

3.11 **Total organic carbon**

Total organic carbon was included in this intercomparison, and the results are presented in Figure 11. The great circle is representing the target acceptance limit of ± 20 %. The reported values from 35 laboratories are given in Table 5.10. Combustion methods are used by most of the laboratories, only five laboratories used UV/peroxodisulfate oxidation method for this determination. The deviations observed in Figure 10 are mainly of systematic nature. The combustion method gives a little higher average than the UV/peroxodisulfate technicque. This time 83 % of the result pairs are considered acceptable, which is rather good.

3.12 **Aluminium**

The results for aluminium are illustrated in Figure 12, and the values reported by the participants are given in Table 5.12. The target accuracy is ± 20 %, and is represented by the great circle in Figure 11. 77 % of the result pairs are located inside this circle. 30 laboratories submitted results for iron, of which 15 and 10 used ICP-AES and ICP-MS, respectively, while only 1 and 4 used flame and graphite furnace atomic absorption, respectively. As for the other

metals the ICP emission methods are clearly taking over more and more on behalf of the atomic absorption methods.

The deviating results are mainly affected by systematic errors. There is not observed any statistically significant difference between the results determined by the different methods for iron.

3.13 **Iron**

The results for iron are illustrated in Figure 13, and the values reported by the participants are given in Table 5.13. The target accuracy is ± 20 %, and is represented by the great circle in Figure 13. This time, 81 % of the result pairs are located inside this circle, which is better than the last intercomparison. 37 laboratories submitted results for iron, of which 18 and 12 used ICP-AES and ICP-MS, respectively, while 4 and 3 used flame and graphite furnace atomic absorption, respectively.

The deviating results are mainly affected by systematic errors. There is observed greater deviations for the atomic absorption methods. The Youden plot looks a little strange this time, because the concentrations in the two samples of the sample pair are very different.

3.14 **Manganese**

The manganese results are illustrated in Figure 14, and the values reported by the participants are given in Table 5.14. The target accuracy is ± 20 %, and is represented by the great circle in Figure 14. This time 85 % of the result pairs are located inside this circle, which is very good. 40 laboratories submitted results for manganese, of which 18 and 14 used ICP-AES and ICP-MS, respectively, while 3 and 5 used flame and graphite furnace atomic absorption, respectively.

3.15 **Cadmium**

The results for cadmium are illustrated in Figure 15, and the values reported by the participants are given in Table 5.15. The target accuracy is ± 20 % and is represented by the great circle in Figure 15. 88 % of the result pairs are located inside this circle, which is very good. 40 laboratories submitted results for cadmium, of which 8 and 20 used ICP-AES and ICP-MS, respectively, while 11 used graphite furnace atomic absorption, and one flame atomic absorption.

3.16 **Lead**

The results for lead are illustrated in Figure 16, and the values reported by the participants are given in Table 5.16. The target accuracy is ± 20 %, and is represented by the great circle in Figure 16. 73 % of the result pairs are located inside this circle, which is the same as at the last intercomparison. 41 laboratories submitted results for lead, of which 8 and 20 used ICP-AES and ICP-MS, respectively, while 12 used graphite furnace atomic absorption. Flame

atomic absorption was used by one laboratory, even though the method is not very sensitive and is not suitable for determination of the lowest lead concentration.

3.17 **Copper**

The copper results are illustrated in Figure 17, and the values reported by the participants are given in Table 5.17. The target accuracy is ± 20 %, and is represented by the great circle in Figure 17. The low number of results being located inside this circle this time, 51 %, is probably caused by the very low concentrations used for copper in sample C. 41 laboratories submitted results for copper, of which 10 used ICP-AES and 20 used ICP-MS, while 9 and 2 used graphite furnace and flame atomic absorption, respectively. Ten laboratories had problems with the sensitivity of the method, especially for sample C with the lowest concentration, and reported “less than” their detection limit.

3.18 **Nickel**

The results for nickel are illustrated in Figure 18, and the values reported by the participants are given in Table 5.18. The target accuracy is ± 20 %, and is represented by the great circle in Figure 18. This time, only 66 % of the result pairs are located inside this circle, which is lower than the last intercomparison, and the main reason for this situation is that the nickel concentrations are lower this time. 38 laboratories submitted results for nickel, of which 9 and 19 used ICP-AES and ICP-MS, respectively, while 9 laboratories used graphite furnace atomic absorption, and one flame atomic absorption.

3.19 **Zinc**

The results for zinc are illustrated in Figure 19, and the values reported by the participants are given in Table 5.19. The target accuracy is ± 20 %, and is represented by the great circle in Figure 19. 82 % of the result pairs are located inside this circle. 38 laboratories submitted results for zinc, of which 13 used ICP-AES and 19 ICP-MS, respectively, while 3 and 3 used flame and graphite furnace atomic absorption, respectively. Generally, the deviating results are affected mainly by systematic errors.

Continue page 37

Table 1. Statistical summary for intercomparison 0923

Analytical variable and method	Sample pair	True value 1	True value 2	Total number	Labs. excl.	Median 1	Median 2	Average Sample 1	Std.dev. Sample 1	Average Sample 2	Std.dev. Sample 2	Rel std.dev. % 1	Rel std.dev. % 2	Relative err. % 1	Relative err. % 2
pH	AB	6,36	6,57	61	0	6,36	6,57	6,33	0,27	6,59	0,26	4,3	3,9	-0,5	0,3
Electrometry				34	0	6,37	6,60	6,40	0,21	6,63	0,23	3,3	3,4	0,6	0,9
Stirring				26	0	6,35	6,54	6,23	0,32	6,52	0,28	5,1	4,2	-2,0	-0,7
Equilibration				1	0			6,57		6,99				3,3	6,4
Conductivity	AB	2,94	4,60	62	7	2,94	4,60	2,93	0,09	4,59	0,16	3,1	3,5	-0,2	-0,3
Alkalinity	AB	0,124	0,220	43	7	0,124	0,220	0,122	0,017	0,219	0,017	13,9	7,9	-1,2	-0,6
Gran plot titration				20	3	0,125	0,221	0,123	0,018	0,222	0,011	14,8	4,8	-0,5	1,0
Two end point				12	1	0,125	0,214	0,123	0,012	0,216	0,010	10,0	4,5	-0,9	-1,7
End p. 5.4				3	0	0,107	0,208	0,106	0,011	0,210	0,013	10,4	6,0	-14,2	-4,7
Other end p.				8	3	0,120	0,218	0,128	0,023	0,217	0,042	18,0	19,2	3,1	-1,3
Nitrate + nitrite-nitrogen	AB	86	46	58	15	86	46	84	10	45	8	12,3	18,7	-1,8	-2,4
Autoanalyzer				14	2	87	46	85	10	45	4	11,2	9,9	-0,7	-2,1
Photometry				9	3	81	47	75	12	45	12	15,8	26,8	-12,6	-1,9
Ion chromatography				33	9	89	45	86	10	45	9	11,3	21,0	0,4	-2,8
Hydrazine				2	1			81		46				-5,8	0,0
Chloride	AB	1,40	4,27	57	8	1,40	4,27	1,41	0,15	4,26	0,27	10,4	6,3	1,0	-0,2
Ion chromatography				51	7	1,40	4,27	1,39	0,11	4,27	0,28	8,2	6,6	-0,5	-0,1
Argentometry				1	1			0,80		3,30				-42,9	-22,7
Manual, Hg				5	0	1,42	4,22	1,60	0,27	4,22	0,13	16,7	3,2	14,1	-1,3
Sulfate	AB	1,21	2,30	56	4	1,21	2,30	1,22	0,20	2,30	0,27	16,1	11,8	0,8	0,4
Ion chromatography				50	4	1,20	2,29	1,21	0,17	2,28	0,26	14,1	11,5	-0,2	-0,3
Photometry				1	0			0,84		2,03				-30,6	-11,4
Nephelometry				3	0	1,24	2,57	1,31	0,34	2,65	0,22	26,2	8,4	7,9	15,7
ICP-AES				2	0			1,55		2,27				28,1	-0,8

Analytical variable and method	Sample pair	True value 1	True value 2	Total number	Labs. excl.	Median 1	Median 2	Average Sample 1	Std.dev. Sample 1	Average Sample 2	Std.dev. Sample 2	Rel std.dev. % 1	Rel std.dev. % 2	Relative err. % 1	Relative err. % 2
Calcium	AB	1,76	4,72	56	6	1,76	4,72	1,73	0,16	4,70	0,37	9,5	7,9	-1,6	-0,3
FAAS				11	2	1,70	4,67	1,74	0,10	4,70	0,26	5,7	5,5	-0,9	-0,4
ICP-AES				13	0	1,76	4,71	1,75	0,12	4,66	0,23	6,9	5,0	-0,8	-1,4
EDTA				2	1			2,00		4,00				13,6	-15,3
Ion chromatography				27	3	1,75	4,80	1,70	0,20	4,74	0,44	11,8	9,3	-3,6	0,5
ICP-MS				3	0	1,77	4,55	1,83	0,10	4,82	0,47	5,4	9,7	3,8	2,1
Magnesium	AB	0,386	0,423	56	5	0,386	0,423	0,388	0,034	0,437	0,033	8,7	7,5	0,6	3,4
FAAS				11	1	0,385	0,440	0,398	0,029	0,457	0,051	7,3	11,3	3,1	7,9
ICP-AES				13	0	0,386	0,426	0,390	0,022	0,435	0,029	5,5	6,6	1,0	2,9
EDTA				2	1			0,390		0,440				1,0	4,0
Ion chromatography				27	3	0,380	0,422	0,381	0,042	0,430	0,023	11,0	5,3	-1,3	1,6
ICP-MS				3	0	0,395	0,419	0,405	0,017	0,440	0,037	4,1	8,4	4,8	4,1
Sodium	AB	4,17	3,37	57	1	4,17	3,37	4,16	0,25	3,34	0,22	5,9	6,5	-0,1	-0,8
FAAS				9	0	4,07	3,31	4,09	0,36	3,29	0,27	8,9	8,1	-2,0	-2,3
ICP-AES				12	0	4,12	3,33	4,12	0,25	3,29	0,23	6,0	6,9	-1,3	-2,3
AES				6	0	4,22	3,45	4,21	0,30	3,43	0,28	7,1	8,2	1,1	1,9
Ion chromatography				27	1	4,18	3,37	4,18	0,18	3,35	0,17	4,3	5,2	0,3	-0,5
ICP-MS				3	0	4,22	3,30	4,35	0,23	3,46	0,28	5,2	8,0	4,3	2,7
Potassium	AB	0,380	0,225	57	6	0,380	0,225	0,378	0,025	0,226	0,023	6,6	10,3	-0,6	0,3
FAAS				10	0	0,385	0,232	0,379	0,027	0,228	0,035	7,2	15,5	-0,3	1,3
ICP-AES				12	0	0,387	0,233	0,383	0,031	0,231	0,019	8,0	8,3	0,7	2,5
AES				6	2	0,395	0,238	0,388	0,034	0,236	0,016	8,8	6,8	2,0	5,0
Ion chromatography				26	4	0,380	0,220	0,370	0,019	0,218	0,020	5,1	9,3	-2,5	-2,9
ICP-MS				3	0	0,393	0,230	0,394	0,002	0,235	0,009	0,6	3,9	3,8	4,6
Total organic carbon	AB	18,90	5,17	35	4	18,90	5,17	18,63	1,52	5,22	0,64	8,2	12,3	-1,4	0,9
Combustion				30	4	18,98	5,27	18,74	1,55	5,25	0,67	8,3	12,8	-0,9	1,5
UV/peroxodisulphate				5	0	17,40	5,09	18,06	1,38	5,05	0,51	7,6	10,0	-4,5	-2,3

Analytical variable and method		Sample pair	True value 1	True value 2	Total number	Labs. excl.	Median 1	Median 2	Average Sample 1	Std.dev. Sample 1	Average Sample 2	Std.dev. Sample 2	Rel std.dev. % 1	Rel std.dev. % 2	Relative err. % 1	Relative err. % 2
Aluminium		CD	379	141	30	3	379	141	377	33	141	15	8,8	10,4	-0,6	-0,3
	FAAS				1	0			365		140				-3,8	-0,4
	GFAAS				4	1	381	138	363	49	144	23	13,5	16,0	-4,3	2,4
	ICP				15	2	388	146	386	14	145	11	3,7	7,5	2,0	3,1
	ICP-MS				10	0	375	139	370	45	133	15	12,3	11,6	-2,5	-5,7
Iron		CD	525	73	37	6	525	73	524	31	72	6	5,9	7,9	-0,2	-0,9
	FAAS				4	2			531		71				1,2	-3,2
	GFAAS				3	1			586		73				11,6	0,3
	ICP-AES				18	2	530	73	530	17	73	4	3,1	5,6	1,0	0,0
	ICP-MS				12	1	504	73	501	28	72	8	5,6	11,4	-4,5	-1,9
Manganese		CD	20,5	16,8	40	4	20,5	16,8	20,2	1,3	16,6	1,2	6,4	6,9	-1,5	-1,1
	FAAS				3	1			20,0		16,2				-2,7	-3,6
	GFAAS				5	1	19,4	17,4	18,9	1,9	17,9	1,6	10,0	9,2	-7,7	6,3
	ICP-AES				18	2	21,0	16,9	20,5	1,4	16,5	1,1	6,7	6,9	0,2	-1,6
	ICP-MS				14	0	20,1	16,8	20,2	0,9	16,4	0,9	4,6	5,8	-1,5	-2,2
Cadmium		CD	4,00	5,77	40	4	4,00	5,77	3,95	0,22	5,76	0,36	5,5	6,2	-1,2	-0,1
	FAAS				1	0			4,03		5,89				0,8	2,1
	GFAAS				11	2	3,79	5,71	3,84	0,22	5,57	0,28	5,8	5,0	-3,9	-3,5
	ICP-AES				8	1	3,90	5,70	3,86	0,30	5,87	0,56	7,8	9,5	-3,6	1,7
	ICP-MS				20	1	4,06	5,89	4,03	0,15	5,81	0,28	3,7	4,9	0,8	0,7
Lead		CD	4,54	6,74	41	6	4,54	6,74	4,53	0,37	6,73	0,66	8,3	9,8	-0,3	-0,2
	FAAS				1	0			4,30		6,18				-5,3	-8,3
	GFAAS				12	2	4,56	6,72	4,47	0,45	6,89	0,99	10,2	14,4	-1,5	2,2
	ICP-AES				8	3	4,43	6,70	4,48	0,45	6,54	0,67	10,1	10,2	-1,3	-2,9
	ICP-MS				20	1	4,59	6,80	4,58	0,33	6,73	0,43	7,2	6,4	0,9	-0,2

Analytical variable and method		Sample pair	True value 1	True value 2	Total number	Labs. excl.	Median 1	Median 2	Average Sample 1	Std.dev. Sample 1	Average Sample 2	Std.dev. Sample 2	Rel std.dev. % 1	Rel std.dev. % 2	Relative err. % 1	Relative err. % 2
Copper		CD	1,10	5,60	41	14	1,10	5,60	1,07	0,14	5,57	0,52	13,4	9,4	-2,5	-0,5
	FAAS				2	1			1,16		5,83				5,5	4,1
	GFAAS				9	4	1,00	4,90	1,08	0,21	5,18	0,93	19,4	17,9	-1,6	-7,5
	ICP-AES				10	6	1,08	5,47	1,09	0,09	5,41	0,46	8,4	8,5	-0,8	-3,4
	ICP-MS				20	3	1,10	5,66	1,06	0,14	5,71	0,33	13,4	5,8	-3,6	2,0
Nickel		CD	4,52	5,59	38	7	4,52	5,59	4,50	0,46	5,50	0,48	10,2	8,8	-0,4	-1,7
	FAAS				1	0			4,71		5,82				4,2	4,1
	GFAAS				9	2	4,33	5,29	4,56	0,66	5,21	0,65	14,4	12,4	0,8	-6,7
	ICP-AES				9	4	4,52	5,50	4,21	0,66	5,36	0,61	15,6	11,5	-6,9	-4,2
	ICP-MS				19	1	4,56	5,60	4,55	0,30	5,63	0,33	6,5	5,9	0,6	0,6
Zinc		CD	26,1	31,5	38	0	26,1	31,5	26,3	2,7	30,8	3,4	10,1	11,1	0,7	-2,4
	FAAS				3	0	22,0	32,0	23,5	4,0	30,4	4,7	17,1	15,6	-9,8	-3,6
	GFAAS				3	0	24,8	23,0	25,5	3,8	24,9	3,5	15,1	13,9	-2,4	-21,0
	ICP-AES				13	0	25,7	31,0	25,6	2,4	30,2	3,3	9,4	10,9	-1,9	-4,2
	ICP-MS				19	0	26,9	32,1	27,3	2,1	32,1	2,2	7,7	7,0	4,7	2,1

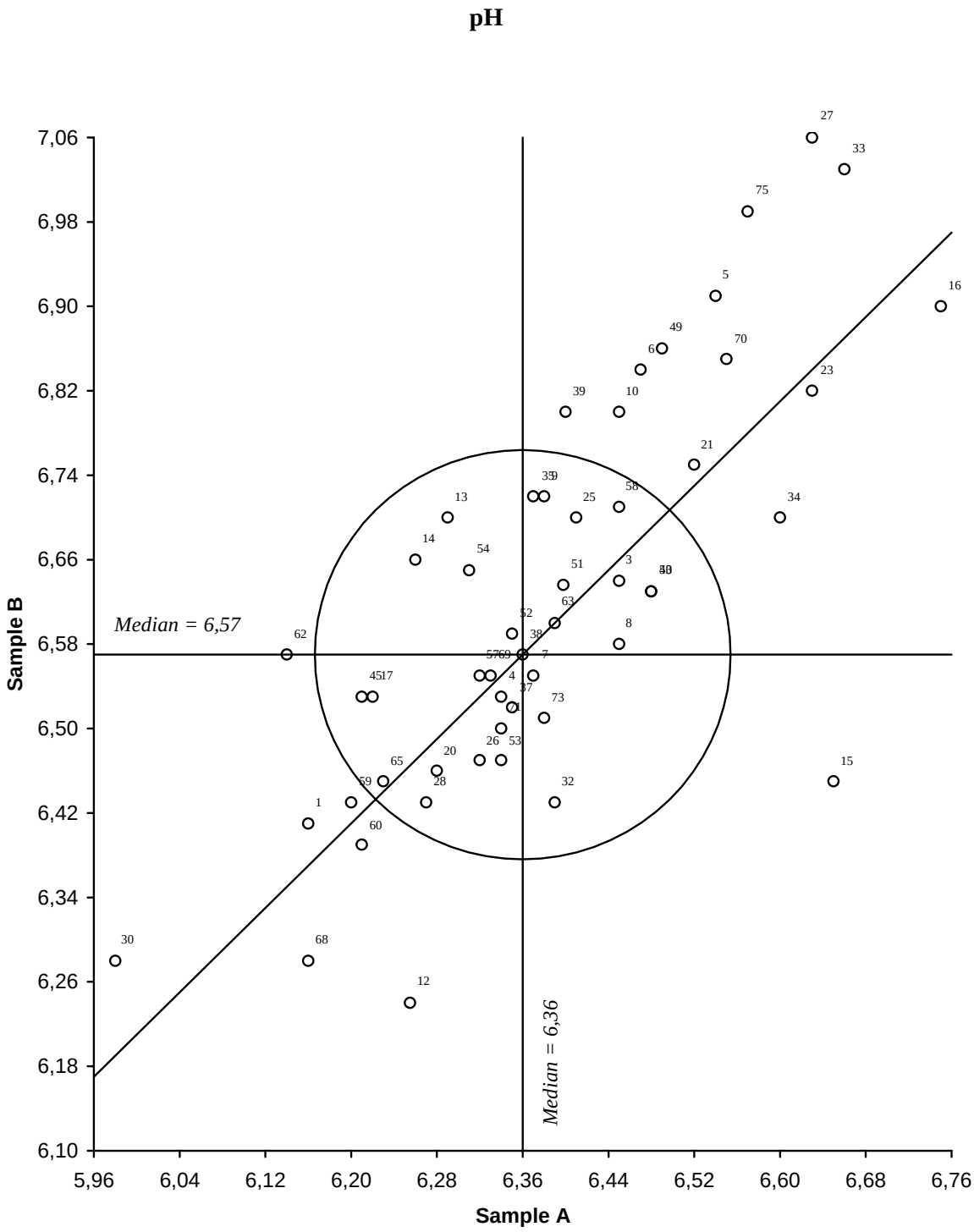

Figure 1. Youden diagramme for pH, sample pair AB
Acceptance limit, given by the circle, is 0,2 pH units

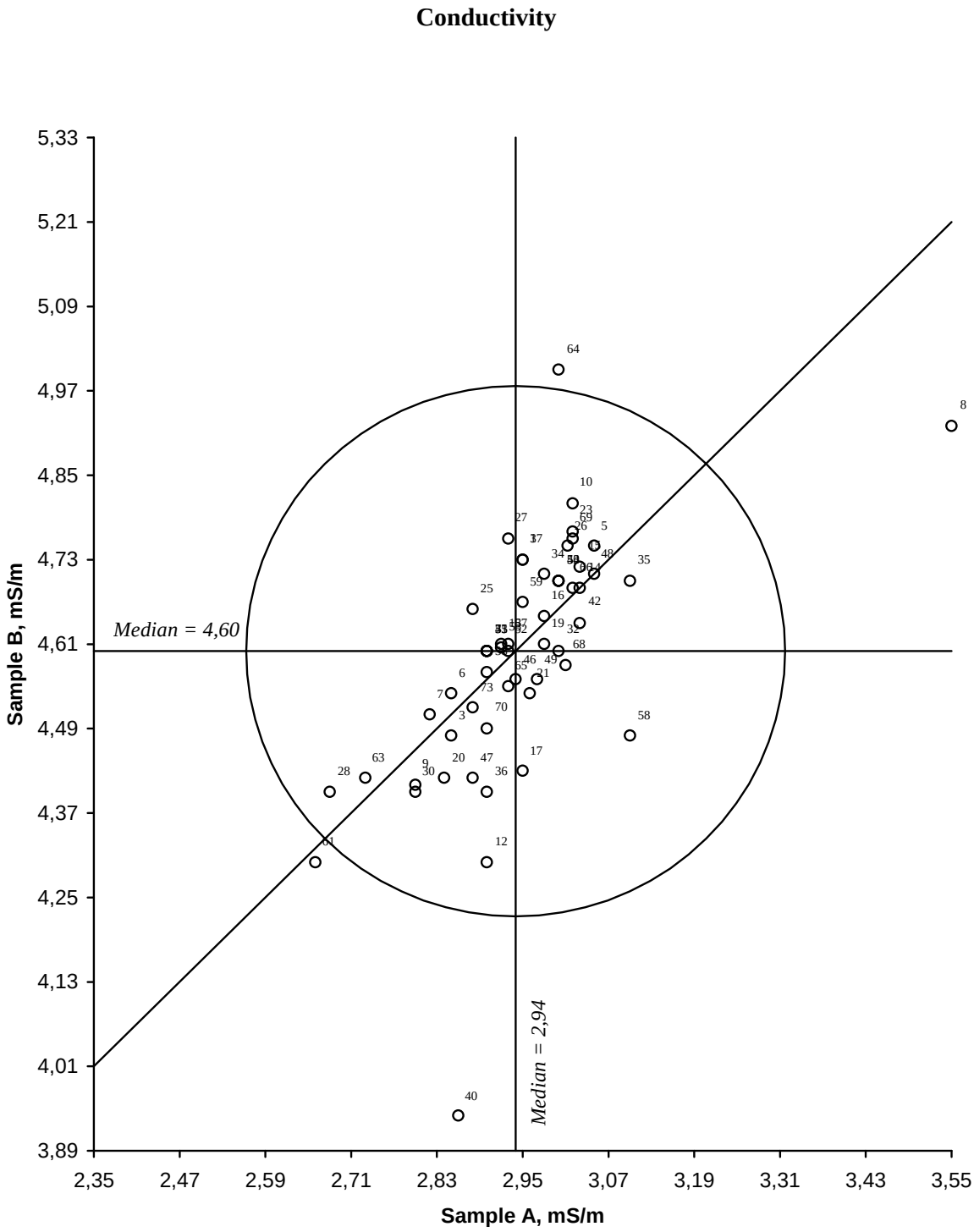

Figure 2. Youden diagramme for conductivity, sample pair AB
Acceptance limit, given by the circle, is 10 %

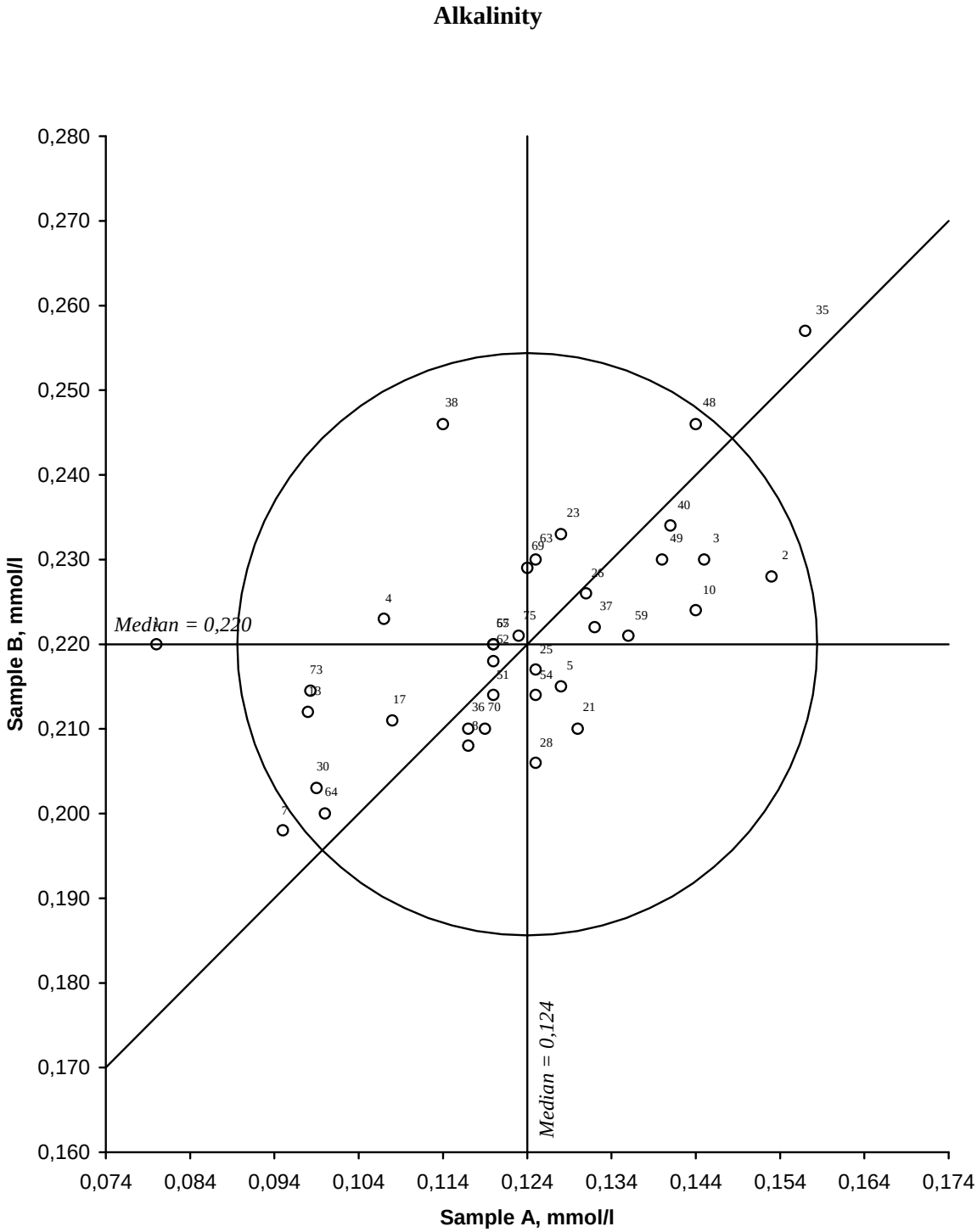

Figure 3. Youden diagramme for alkalinity, sample pair AB
Acceptance limit, given by the circle, is 20 %

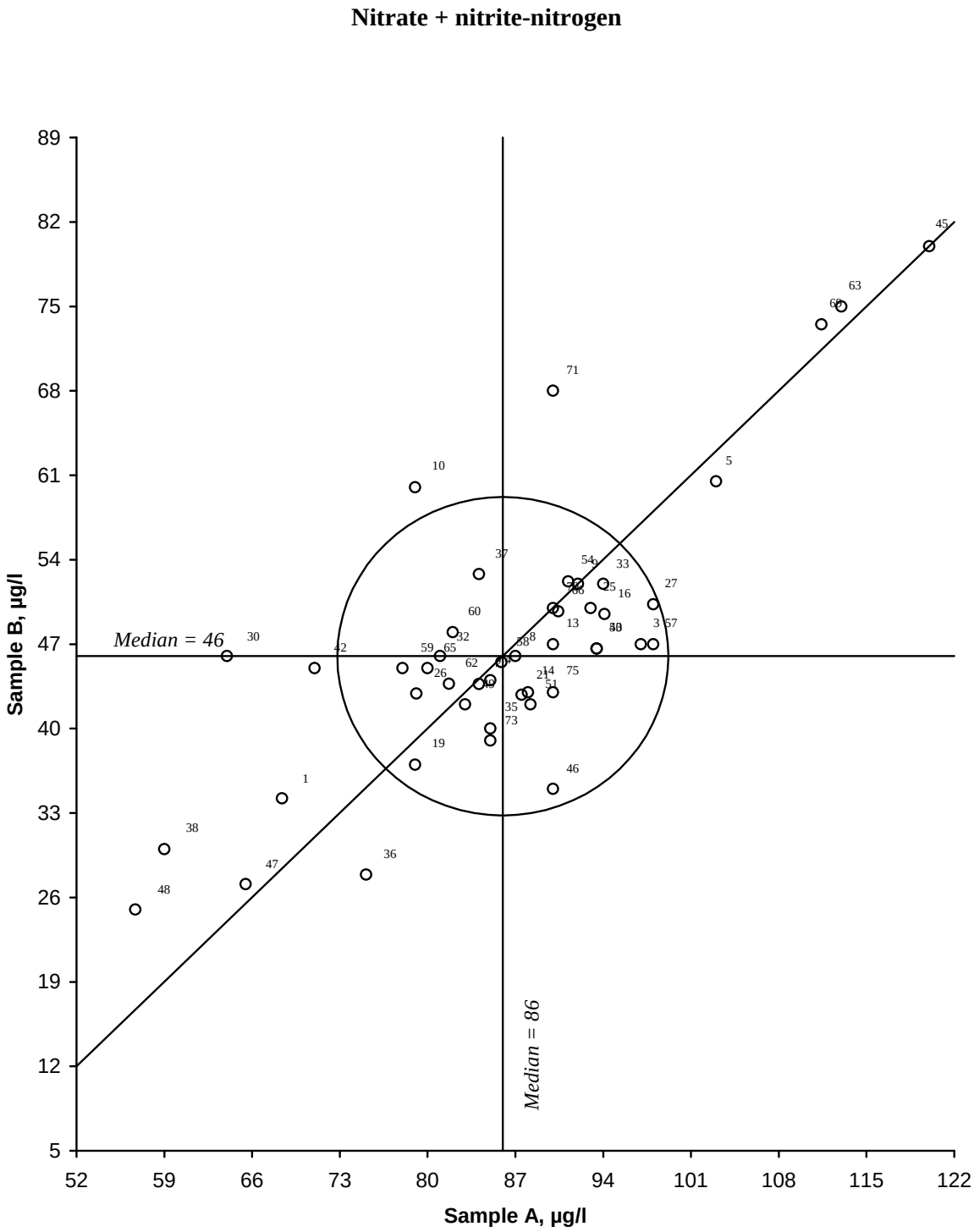

Figure 4. Youden diagramme for nitrate + nitrite-nitrogen, sample pair AB
Acceptance limit, given by the circle, is 20 %

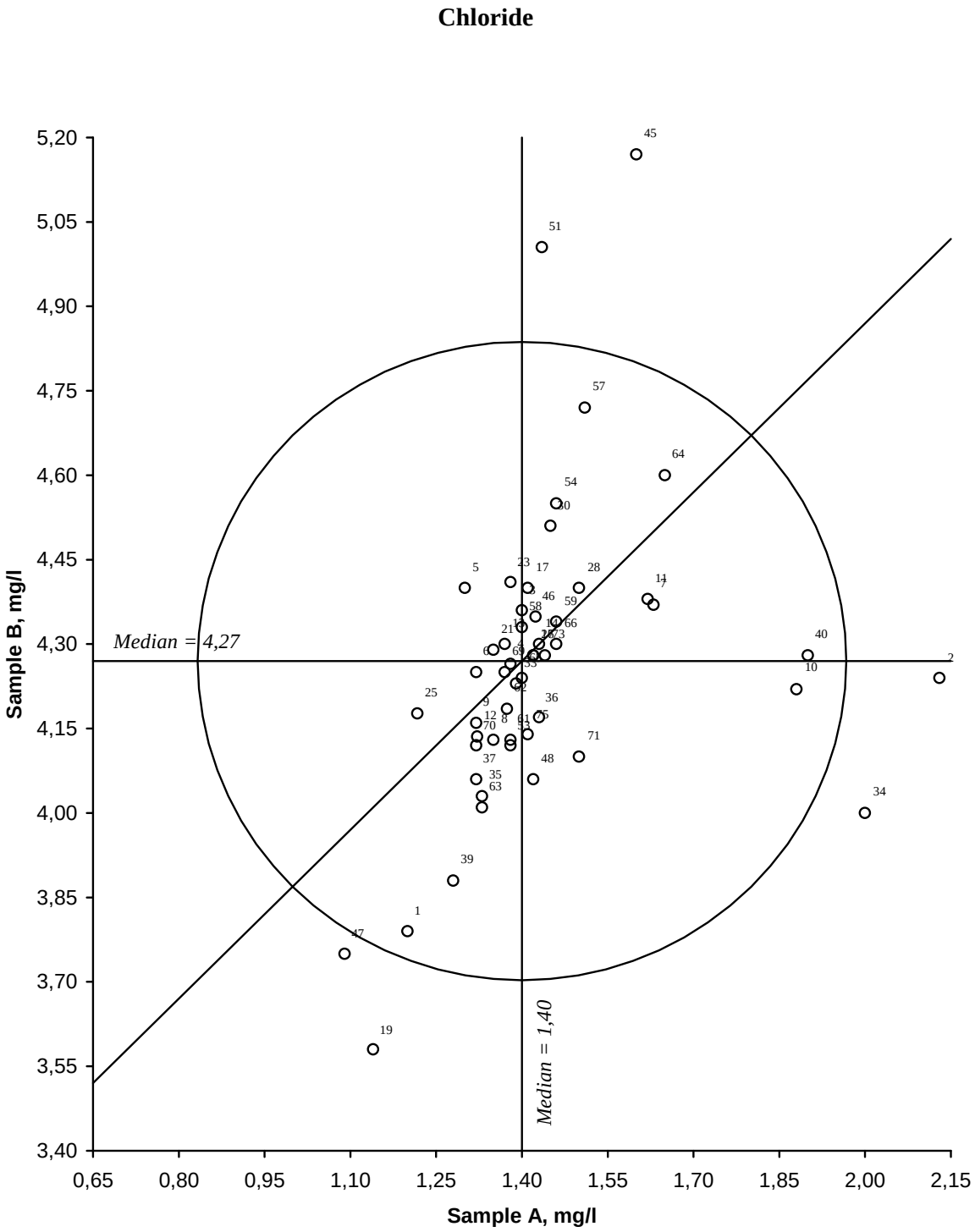

Figure 5. Youden diagramme for chloride, sample pair AB
Acceptance limit, given by the circle, is 20 %

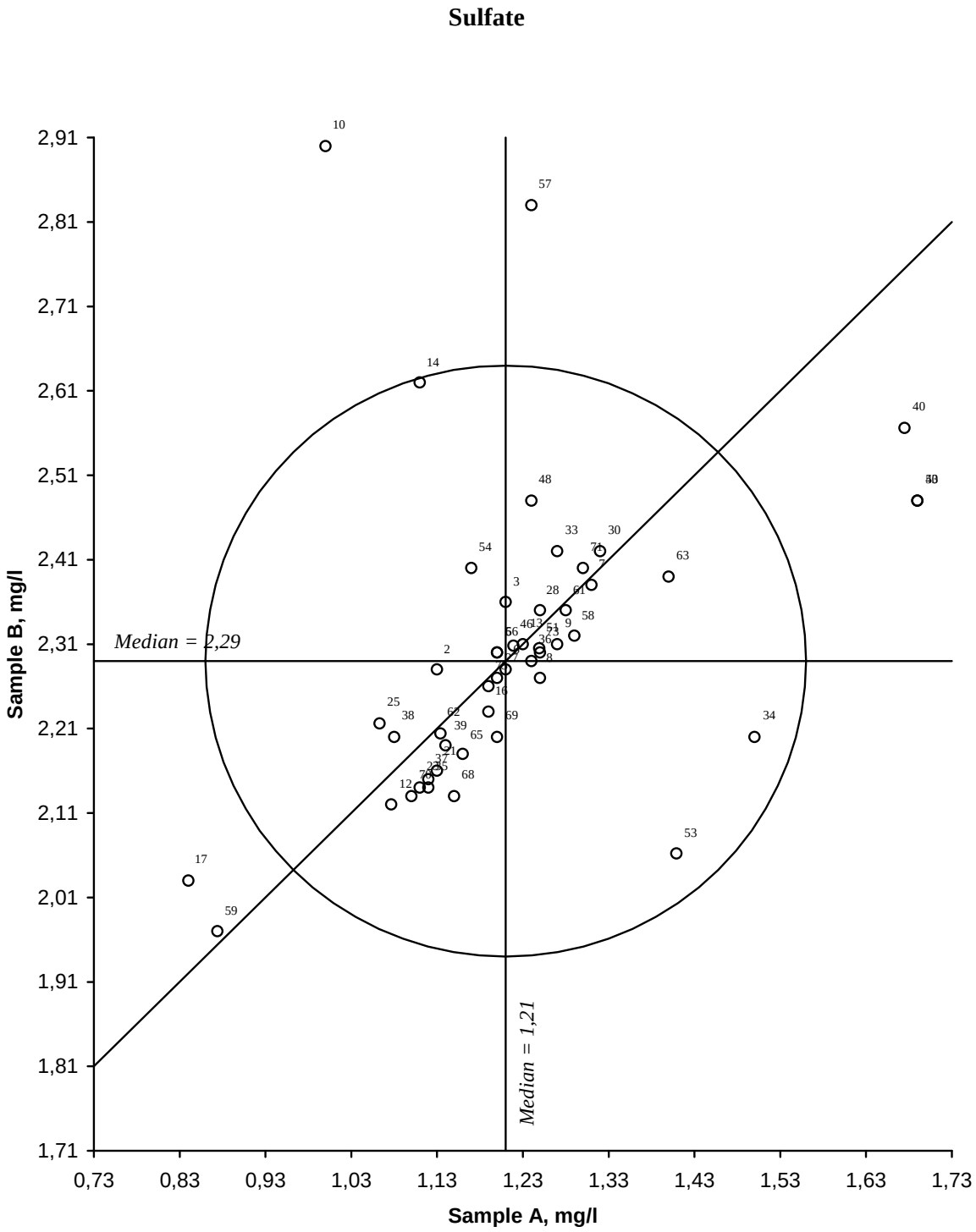

Figure 6. Youden diagramme for sulfate, sample pair AB
Acceptance limit, given by the circle, is 20 %

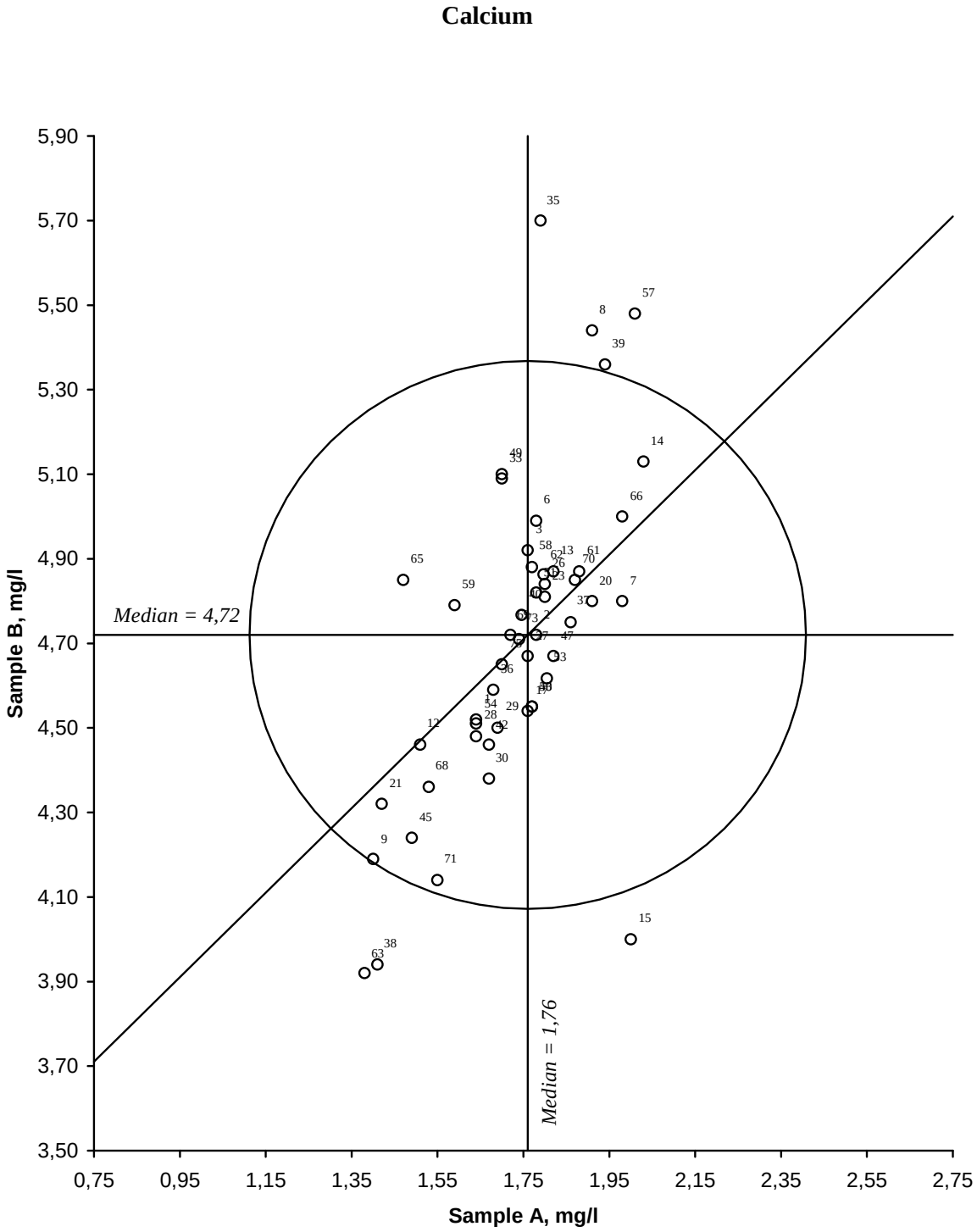

Figure 7. Youden diagramme for calcium, sample pair AB
Acceptance limit, given by the circle, is 20 %

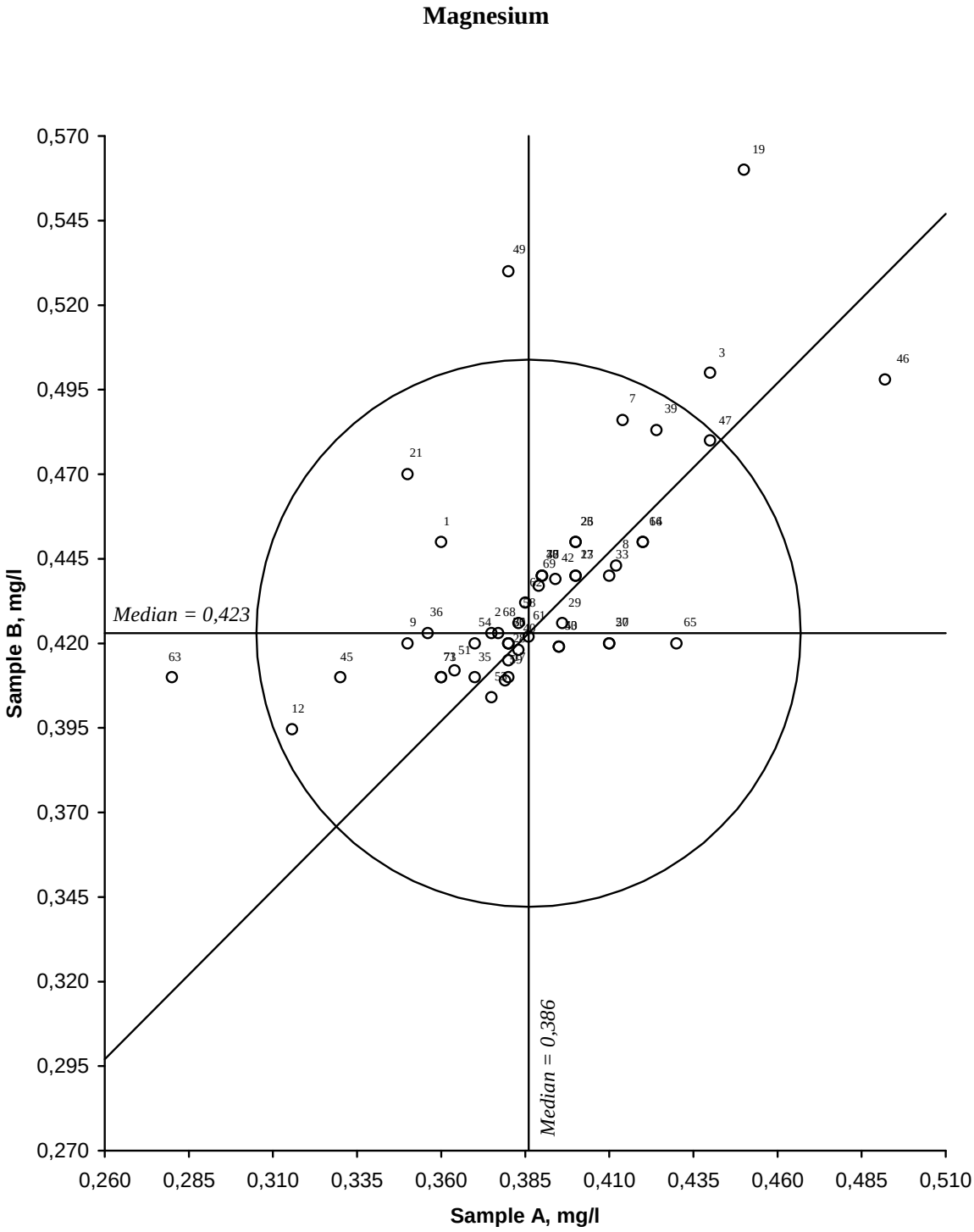

Figure 8. Youden diagramme for magnesium, sample pair AB
Acceptance limit, given by the circle, is 20 %

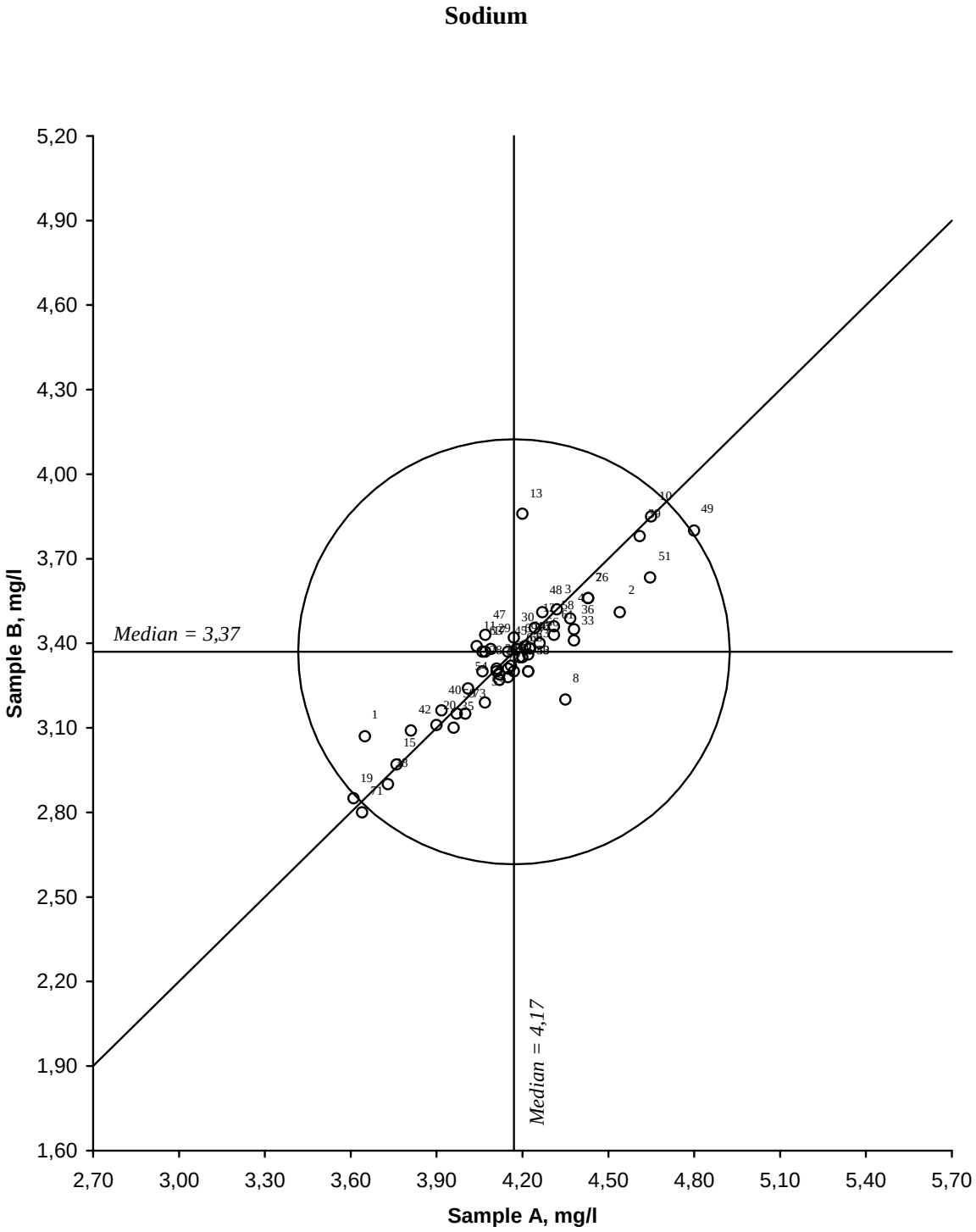

Figure 9. Youden diagramme for sodium, sample pair AB
Acceptance limit, given by the circle, is 20 %

Potassium

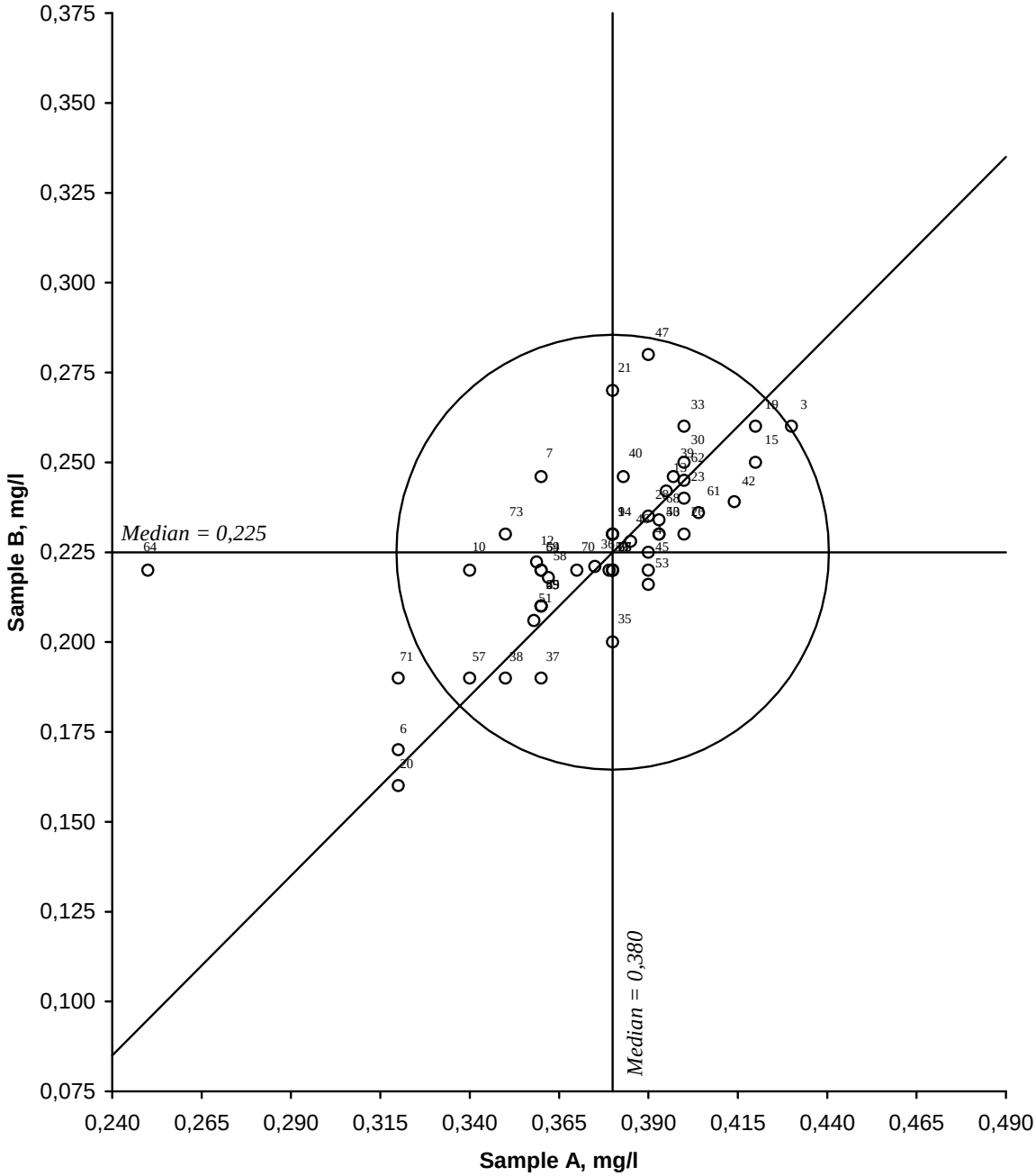

Figure 10. Youden diagramme for potassium, sample pair AB
Acceptance limit, given by circle, is 20 %

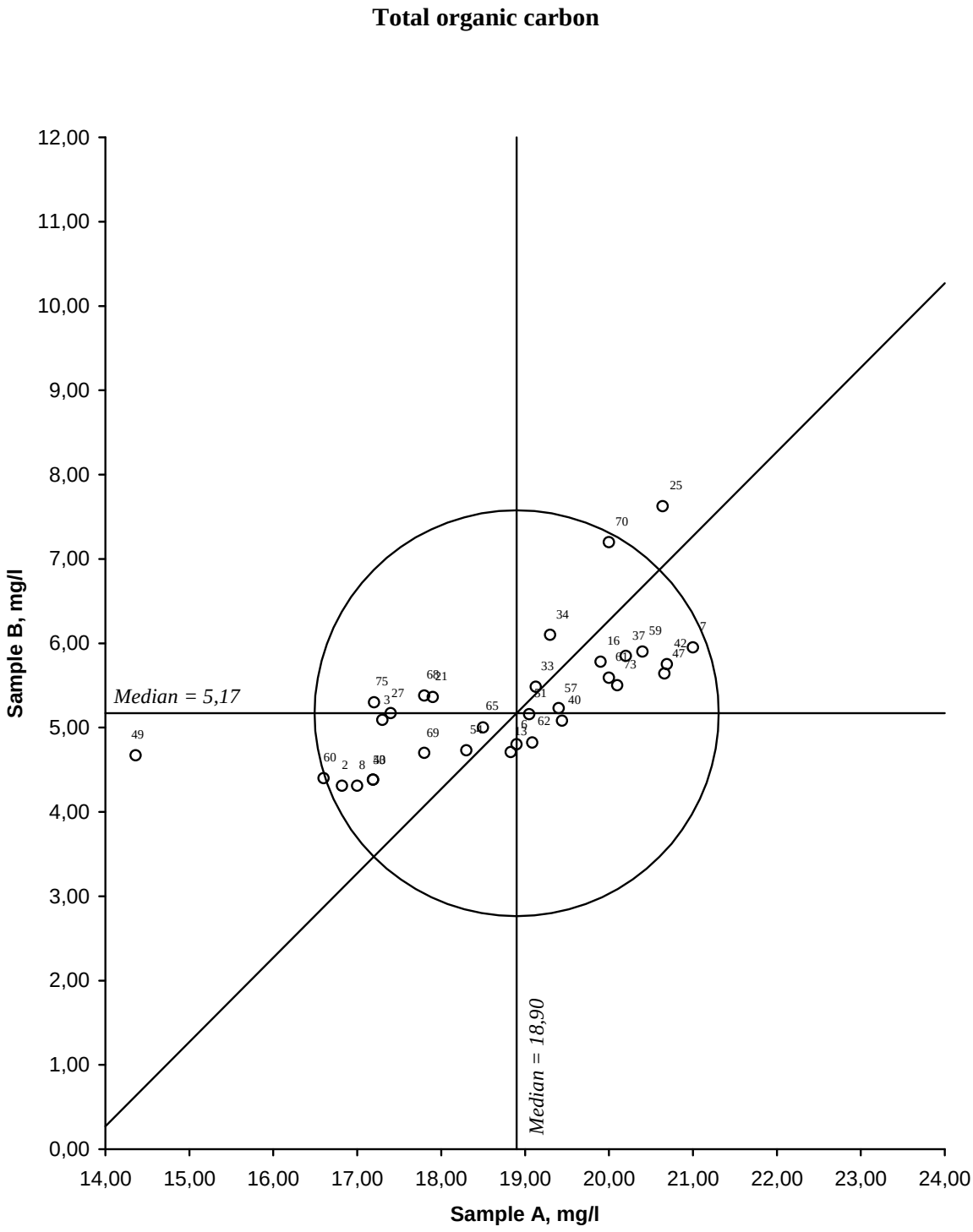

Figure 11. Youden diagramme for total organic carbon, sample pair AB
Acceptance limit, given by the circle, is 20 %

Aluminium

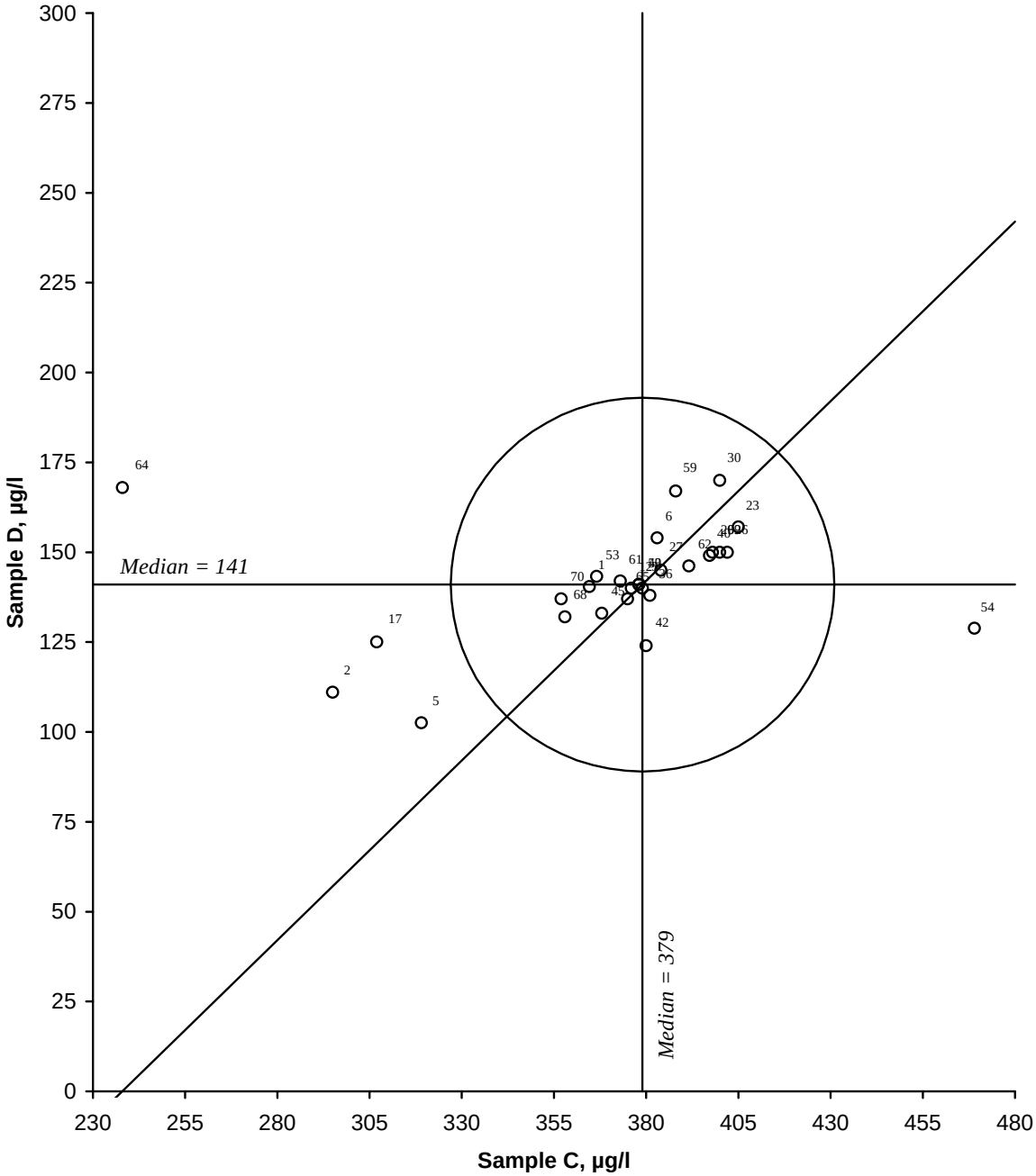

Figure 12. Youden diagramme for aluminium, sample pair CD
Acceptance limit, given by the circle, is 20 %

Iron

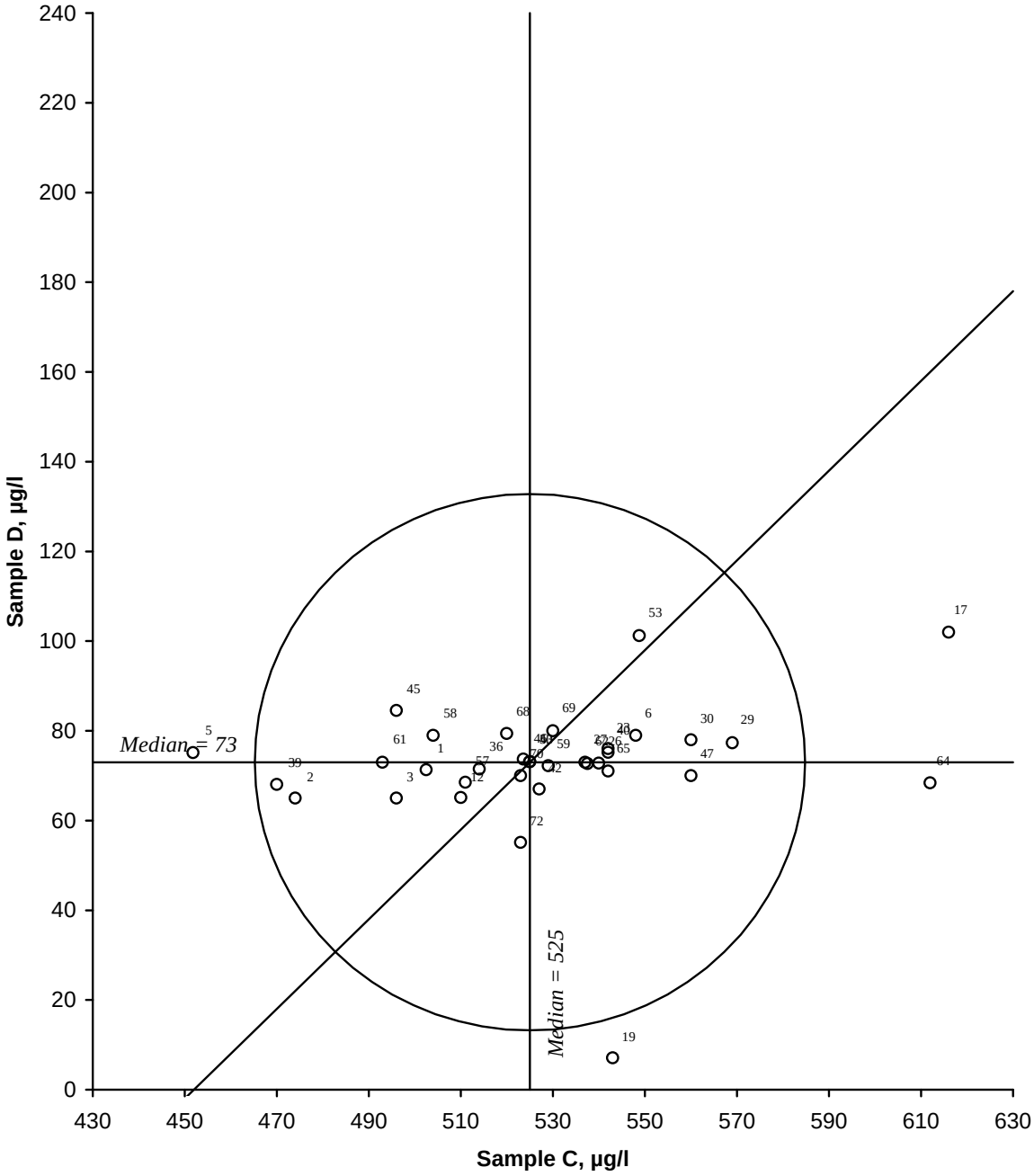

Figure 13. Youden diagramme for iron, sample pair CD
Acceptance limit, given by the circle, is 20 %

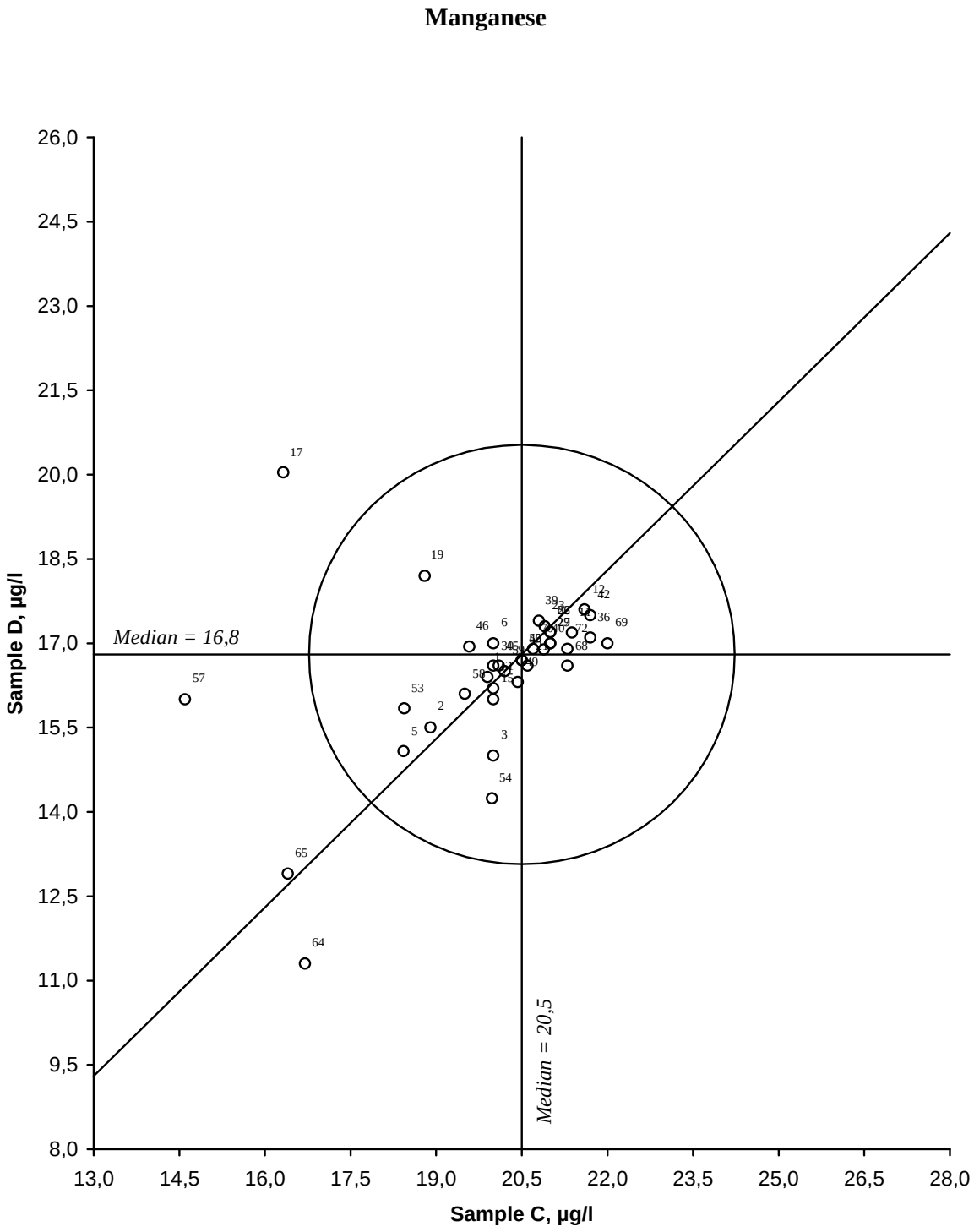

Figure 14. Youden diagramme for manganese, sample pair CD
Acceptance limit, given by the circle, is 20 %

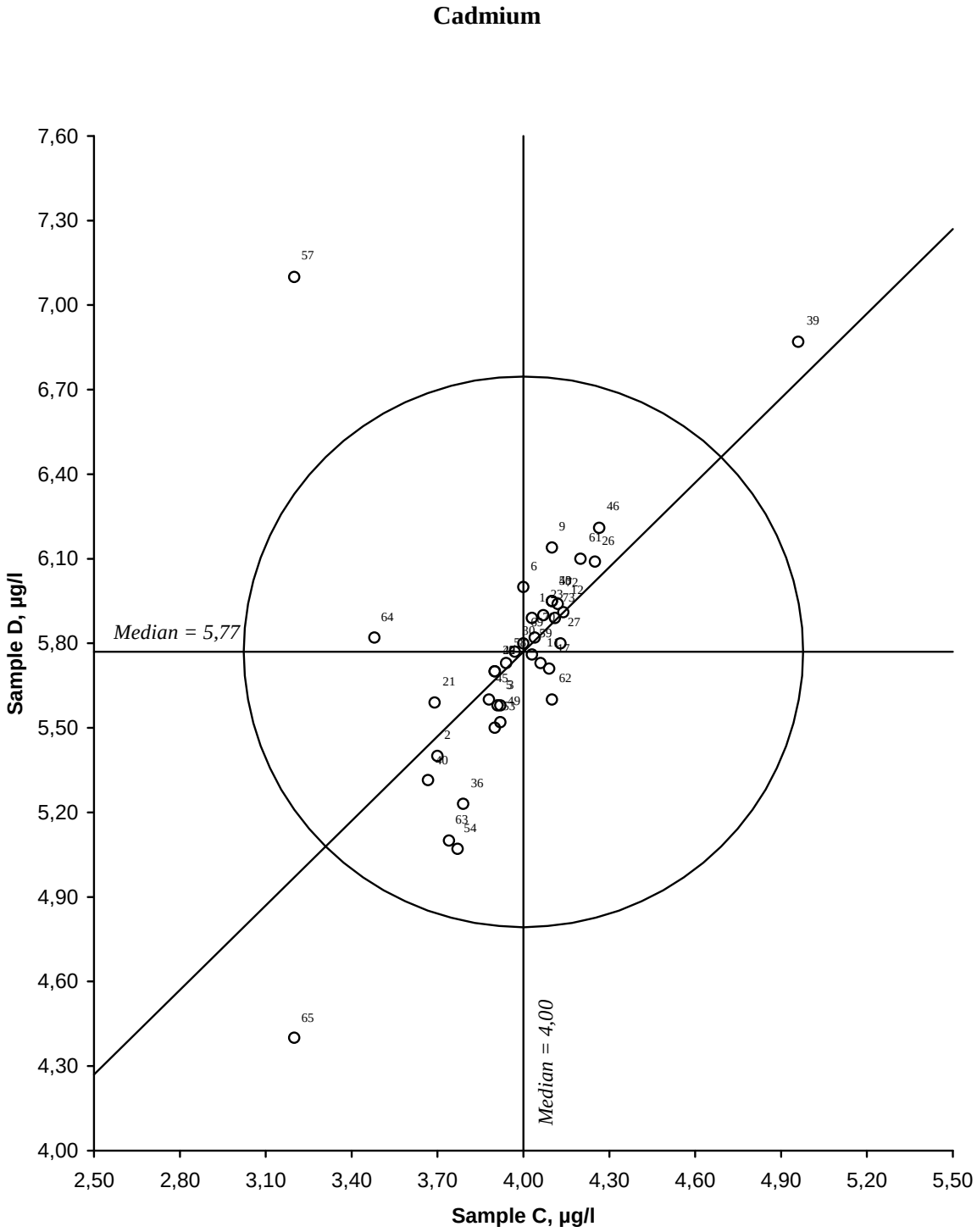

Figure 15. Youden diagramme for cadmium, sample pair CD
Acceptance limit, given by the circle, is 20 %

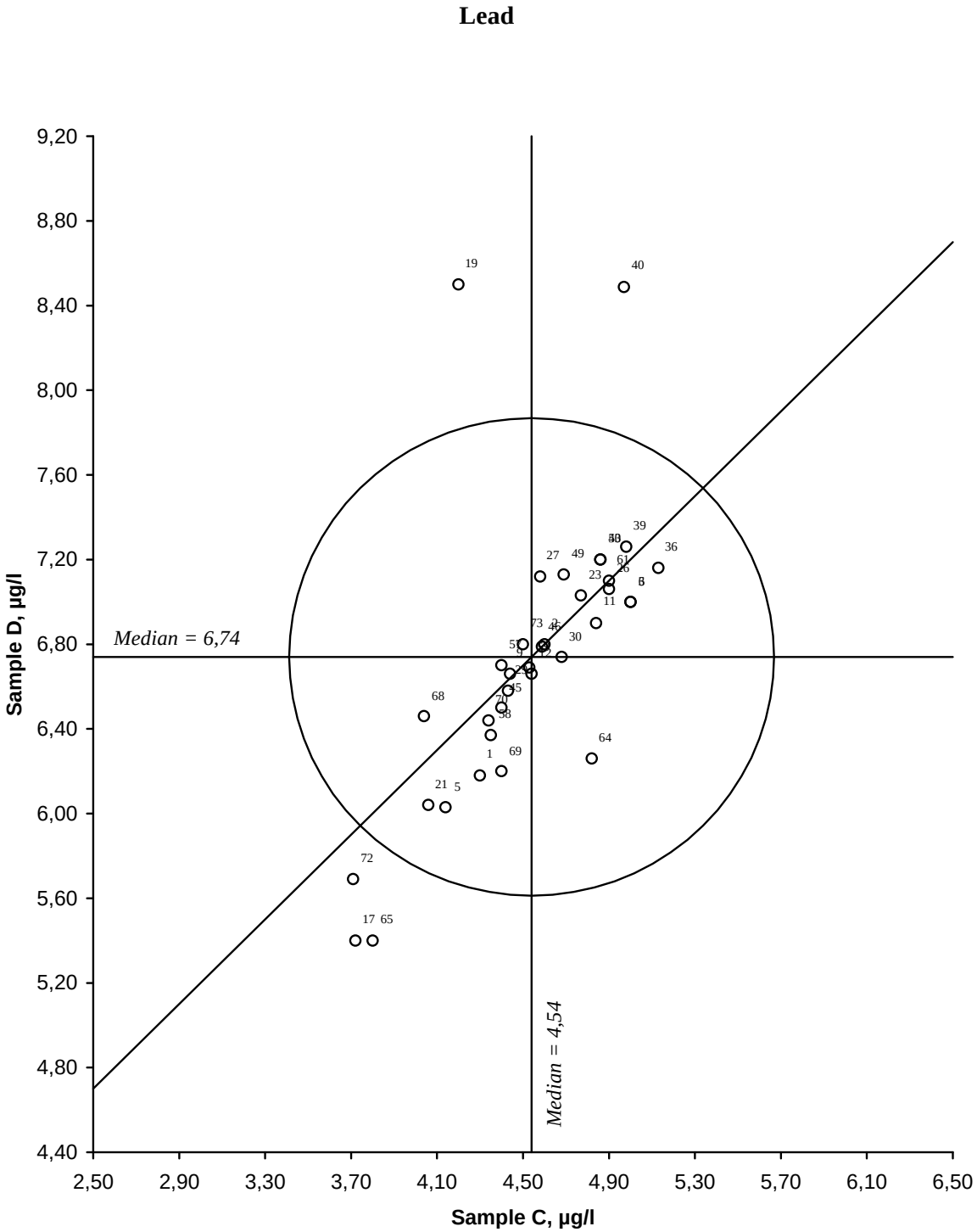

Figure 16. Youden diagramme for lead, sample pair CD
Acceptance limit, given by circel, is 20 %

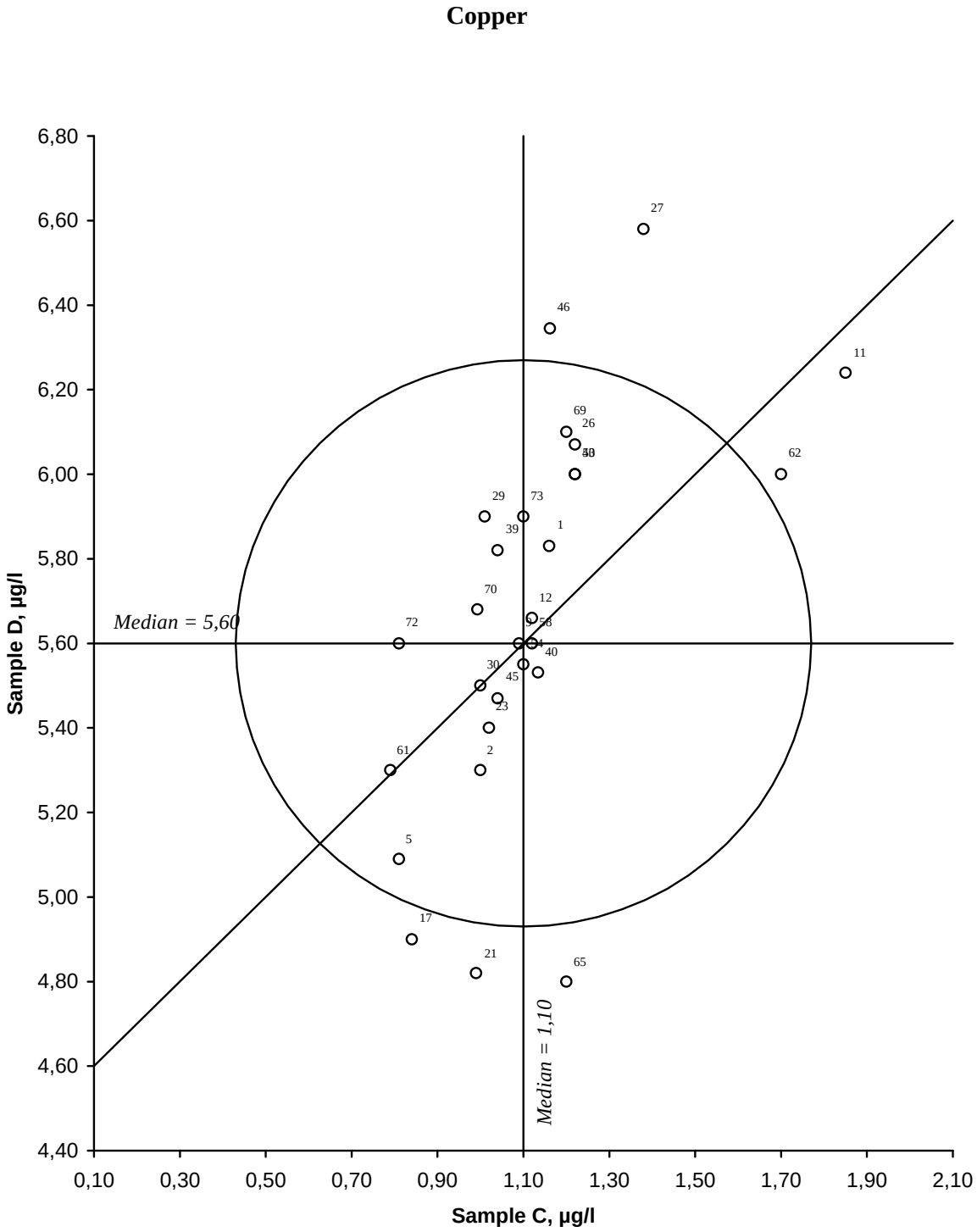

Figure 17. Youden diagramme for copper, sample pair CD
Acceptance limit, given by the circle, is 20 %

Nickel

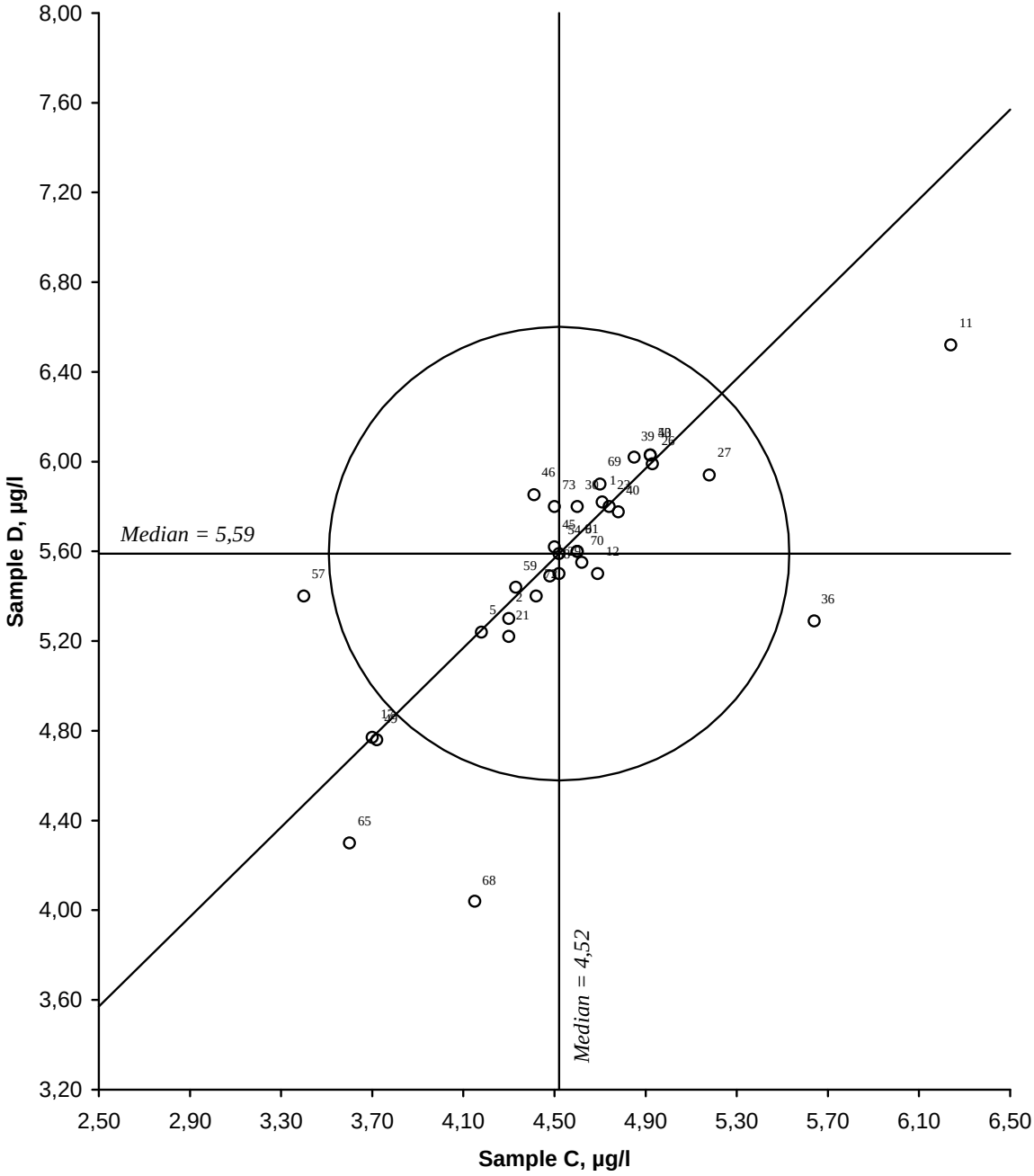

Figure 18. Youden diagramme for nickel, sample pair CD
Acceptance limit, given by the circle, is 20 %

Zinc

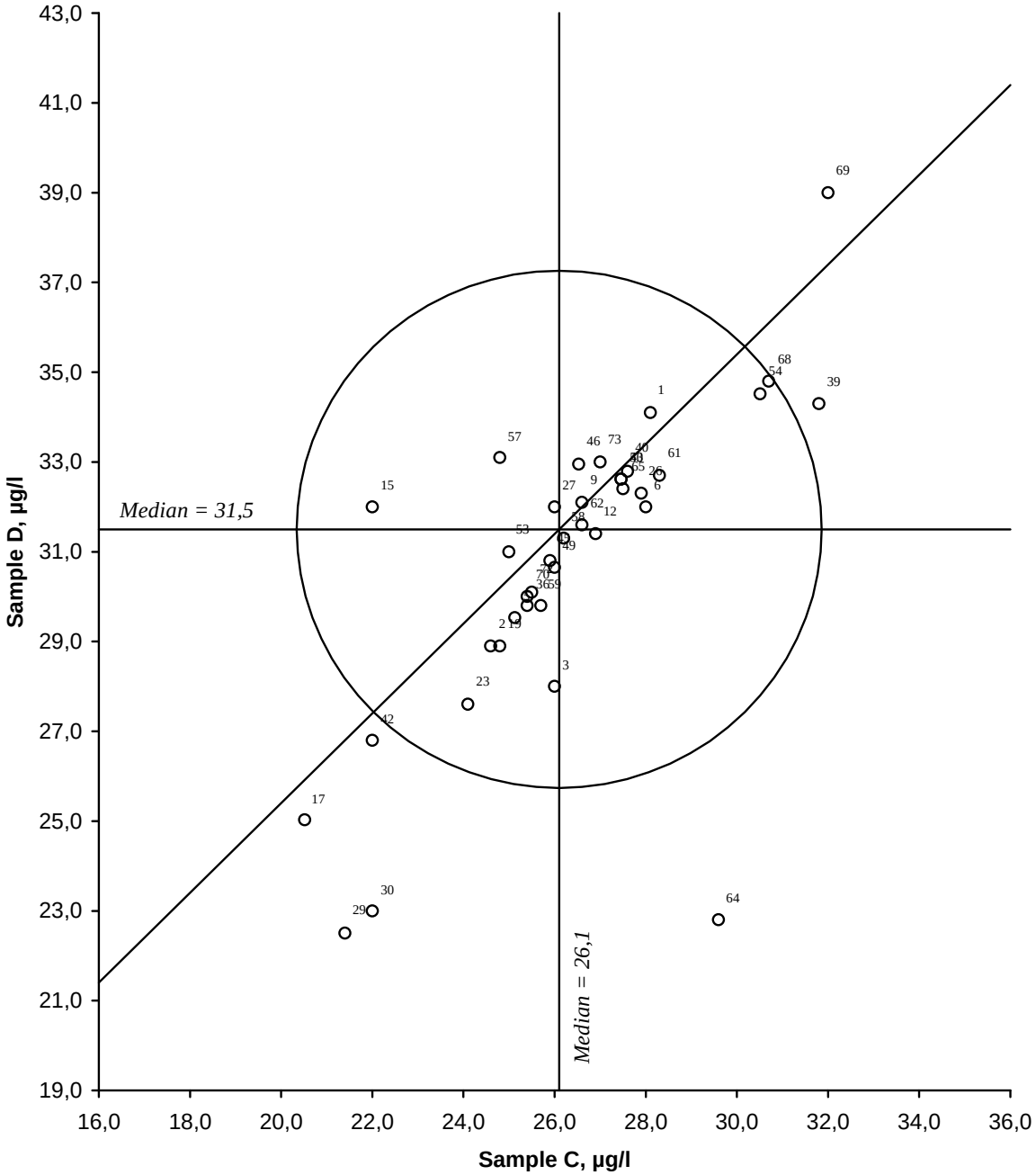

Figure 19. Youden diagramme for zinc, sample pair CD
Acceptance limit, given by the circle, is 20 %

4. Discussion

The general rule for target accuracies, outlined in the Manual for Chemical and Biological Monitoring (1), shall normally be used as acceptance limits for the results of the intercomparison test. These limits are corresponding to either the detection limit of the method, or 20 % of the true value, whichever being the greater, i.e. fixed or relative acceptance limits.

In Table 2 an evaluation of the results of intercomparison 1024 is presented, based on the target accuracy (except for pH and conductivity), where the number and percentage of acceptable results are given. 75 % of the results submitted by the participants are acceptable when compared to the acceptance limits given above. By improvement of the routine analytical method, the laboratories should be able to obtain even more accurate and comparable results.

In table 4 (page 47) the individual results of each laboratory are given. The results reported by the laboratory are printed, however, in some cases the result has been enhanced to one more digit than is statistically significant. There are some laboratories using far more digits than are statistically significant. This is absolutely unnecessary, and each laboratory should determine how many digits are significant for each of their analytical methods. Of course, one digit more than what is statistically significant can be accepted, this will reduce the round-off error in the statistical calculations of the reported results.

For pH, the general target accuracy is ± 0,1 pH units (1), and less than 50 % of the result pairs are found within these accuracy limits. However, we have chosen to extend the acceptance limit to ± 0,2 pH units. Even with this wider acceptance limit only 49 % of the result pairs are evaluated as acceptable this time.

pH results may be strongly affected by the method used, when the measurement is performed in nearly neutral solutions. This problem has been demonstrated through several earlier intercomparisons, and will remain as a problem as long as different methods, and different working procedures and different instrumental equipment for pH determination are used by the participating laboratories. This time there were only minor differences between the pH results produced during stirring the solution and no stirring of the solution, equilibration of the samples before measurement gave somewhat higher results.

Because of the high precision of the reported results for conductivity in earlier intercomparisons, we have reduced the acceptance limit for this analytical variable from the target value ± 20 % to ± 10 %. Still the number of acceptable results for conductivity is 84 % (Table 2). If we increase the acceptance limit to the target value, the number of acceptable results would increase. For this parameter it is still a problem that many laboratories report their results in the units they normally use at their own laboratory, and they very often do not write the unit used. The unit asked for in this intercomparison is mS/m. For this reason some correspondence with the laboratories was necessary to clarify the right results. In some cases where the laboratory had given the necessary information together with the conductivity results, it was possible to recalculate the results to the unit mS/m.

Continue page 39

Table 2. Evaluation of the results of intercomparison 1024. N is the number of result pairs reported, and n is the number of acceptable results within the given target accuracy.

Parameter and unit	Sample pair	True value 1	True value 2	Accept. limit %	Number of pairs N	Number of pairs n	% acceptable results for intercomparison 1024	0923	0822	0721
pH	AB	6,36	6,57	0,2 *	61	30	**49**	61	68	51
Conductivity, mS/m	AB	2,94	4,6	10	62	52	**84**	71	81	80
Alkalinity, mmol/l	AB	0,124	0,22	20	43	32	**74**	67	35	67
Nitrate + nitrite-N, µg/l	AB	86	46	20	58	33	**57**	58	64	63
Chloride, mg/l	AB	1,4	4,27	20	57	45	**79**	86	85	79
Sulfate, mg/l	AB	1,21	2,29	20	56	41	**73**	77	84	81
Calcium, mg/l	AB	1,76	4,72	20	56	43	**77**	84	85	86
Magnesium, mg/l	AB	0,386	0,423	20	56	46	**82**	88	78	77
Sodium, mg/l	AB	4,17	3,37	20	57	53	**93**	88	91	92
Potassium, mg/l	AB	0,38	0,225	20	57	47	**82**	75	65	77
Total organic C, mg/l	AB	18,9	5,17	20	35	29	**83**	82	-	-
Aluminium, µg/l	CD	379	141	20	30	23	**77**	77	-	-
Iron, µg/l	CD	525	73	20	37	30	**81**	73	83	63
Manganese, µg/l	CD	20,5	16,8	20	40	34	**85**	67	40	70
Cadmium, µg/l	CD	4	5,77	20	40	35	**88**	79	80	75
Lead, µg/l	CD	4,54	6,74	20	41	30	**73**	74	67	64
Copper, µg/l	CD	1,1	5,6	20	41	21	**51**	37	20	82
Nickel, µg/l	CD	4,52	5,59	20	38	25	**66**	85	54	62
Zinc, µg/l	CD	26,1	31,5	20	38	31	**82**	90	62	53
Total					903	680	**75**	(75)	(69)	(73)

* The accepatble limit is extended from the target value of ± 0,1 to ± 0,2 pH units
¤ The accepatble limit is reduced from the target value of ± 20 % to ± 10 %

For alkalinity, as we have observed earlier, the reported results for solutions with low alkalinity values are much more widely spread than are solutions with higher concentrations of bicarbonate. In this intercomparison, the number of acceptable results were 74 %, and a possible explanation for this may be the higher concentrations of bicarbonate in the two samples this time.

For nitrate only 57 % of the result pairs are acceptable. This is too low, and it may perhaps be caused by some unstability for this parameter during transport of the samples. Control analyses at the Programme Centre demonstrated that the samples were not stable enough with respect to the content of nitrate, throughout the whole periode of the intercomparison. Also, some participants pointed out that they observed a certain unstability for this parameter on storage of the samples.

For the major ions, chloride, sulphate, calcium, magnesium and sodium, the number of acceptable results are high as usual. Also the parameter total organic carbon had 83 % acceptable results.

The best results for some heavy metals included in this intercomparison programme were obtained for cadmium and manganese where 88 % and 85 % of the results, respectively, are acceptable. This is considered as acceptable. For some of the elements the concentrations were low, and it is obvious that some laboratories do not have sensitive enough methods to determine heavy metals on the trace level.

It should be discussed what concentration levels for the heavy metals would be most useful for ICP Waters in the coming intercomparisons. It should also be discussed whether *absolute* acceptance limits should be used instead of the *relative* one (± 20 %), which is used in this intercomparison, in cases where the results are close to the detection limit. In such cases it is important that the steering committee decides what target detection limit should be obtained by the participating laboratories.

4. Conclusion

65 laboratories submitted results for this intercomparison. The best results were reported for the analytical variables sodium, cadmium and manganese, where 93 %, 88 % and 85 % of the results, respectively, were acceptable. The worst results were observed for pH with only 49 % acceptable results, and copper where the concentrations are rather low, with only 51 % acceptable results.

In this intecomparison 75 % of the evaluated results were located within the general target accuracy of ± 20 %, or the special accuracy limit for pH and conductivity. The low fraction of acceptable results for some variables may be explained by the rather low concentrations used for these analytical variables and in some cases that the samples were not stable enough. When the concentrations are close to the detection limits for some of the methods used by the participants, it must be expected that the spread of the results will be greater than ± 20 %.

The laboratories which reported results outside this limit should improve their methods to obtain a better accuracy and comparability. Generally, the application of some analytical methods seems to be less suited for the water samples analyzed in this programme, as the detection limits of some methods applied by participants are too high. This is especially true for some manual methods, and some of the methods used for the determination of metals, especially when the concentration is very low. It is important that methods with sufficiently low detection limits are used by the participating laboratories.

A few laboratories do not report the results in the unit requested, in addition they very often do not specify which unit has really been used. It is very important that the unit used is clearly specified.

A total error of ± 0,2 pH units seems to be a reasonable assessment of the accuracy for pH measurements, when near neutral water samples - which are not in CO_2 equilibrium - are analyzed.

Considering the determination of metals in these samples, it is quite clear that the emission techniques (ICP-AES, ICP-MS etc.) are taking over for atomic absorption methods, which were the dominating methods some years ago. For the major ions the ion chromatography technique are clearly growing on behalf of the traditional methods, the photometric methods for the anions and the atomic absorption or emission methods for the cations.

The Youden technique for evaluating intercomparison results presupposes that the two samples in a sample set are comparable with respect to the concentration of each parameter. In this intercomparison there may be a little too big difference between the concentrations of the two samples for some parameters, especially iron and copper. This should be kept in mind when the samples for the next intercomparison is prepared.

5. Literature

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Appendix A.

The participating laboratories

No.	Laboratory	Town	Country
1	Limnological Institute of RAS / SB	Irkutsk	Russia
2	ECOLAB	Tolosan	France
3	University of Maine	Orono	USA
4	IVL AB	Gothenburg	Sweden
5	Charles University	Blatna	Czech Republic
6	Shimane Prefectural Institute of Public Health	Shimane	Japan
7	SLU, Institut for Mark och Miljø	Uppsala	Sweden
8	SLU, Marklaboratoriet, mv-huset	Uppsala	Sweden
9	Environm. Agency of the Republic of Slovenia	Ljubljana	Slovenia
10	Primorsky Department for Hydromet.	Vladivostok	Russia
11	Institute of Environmental Engineering	Zabrze	Poland
12	EPA Dublin Regional Inspectorate	Dublin	Ireland
13	Leopold-Franzeus Universität Innsbruck	Innsbruck	Austria
14	Institute of Meteorology and Geophysics	Innsbruck	Austria
15	Geological Survey of Estonia	Tallinn	Estonia
16	Tallinn University of Technology	Tallinn	Estonia
17	Northern Water Problems Institute	Petrozavodsk	Russia
18	University of Silesia	Sosnowiec	Poland
19	Polish Academy of Sciences	Krakow	Poland
20	Institute of Public Health	Kranj	Slovenia
21	Environmental Protection Agency	Vilnius	Lithuania
22	Institute of Global Climate and Technology	Moscow	Russia
23	Laboratory of Geology and Geography	Helsinki	Finland
24	LOOP P.O.Box 21	Vielha, Lleida	Spain
25	Finnish Forest Research Institute	Rovaniemi	Finland
26	Finnish Environment Institute	Helsinki	Finland
27	Bayerische Landesamt für Umwelt	Munchen	Germany
28	Ontario Ministry of Environment	Dorset	Canada
29	Inst. of North Industrial Ecology, ICPmethods	Apatity	Russia
30	Kola Science Center, INEP	Apatity	Russia
31	Adirondack Lakes Survey Corporation	Ray Brook	USA
32	Freswater Institute, ELE Sattellite Laboratory	Winnipeg	Canada
33	Freswater Institute	Winnipeg	Canada
34	Staatl. Betriebsgesellsch. für Umwelt und Landw.	Chemnitz	Germany
35	National Institute of Biology, LFTER	Ljubljana	Slovenia
36	Institute for Ecology of Industrial Areas	Katowice	Poland
37	KCL Kymen Laboratorio Oy	Kouvola	Finland
38	Laboratorio Biologico Provinciale	Laives	Italy
39	University of Navarra	Pamplona	Spain
40	Institute of Biology, ECOANALYT	Syktyvkar	Russia
41	Institute of Environmental Protection	Warsaw	Poland
42	Finnish Forest research Institute	Vantaa	Finland
43	Environment Agency, Starcross Lab.	Starcross	United Kingdom

No.	Laboratory	Town	Country
44	Umweltbundesamt Austria	Vienna	Austria
45	Norwegian Institute for Air Research	Kjeller	Norway
46	VMM, Afdeling Lucht, Milieu en Communicatie	Antwerpen	Belgium
47	Chemical Laboratory of CGS	Praha Barrandov	Czech Republic
48	Environmental Pollution Monitoring Center	Murmansk	Russia
49	Latvian Environmental Laboratory	Riga	Latvia
50	Environment Agency, NLS Starcross Lab	Exeter	United Kingdom
51	Freshwater Science Laboratory	Pitlochry	Scotland
52	Institute of Environmental Protection	Warsaw	Poland
53	Soil science and forest of temp. and boreal eco.	Goettingen	Germany
54	Acid Deposition and Oxidant Research Center	Niigata-shi	Japan
55	Vlaamse milieumaatschappi	Antwerpen	Belgium
56	Ufficio Protezione Aria	Bellinzona	Switzerland
57	Sezione protezione aria, acqua e suolo	Bellinzona	Switzerland
58	Umweltbundesamt	Langen	Germany
59	Tartu Environmental research	Tartu	Estonia
60	River Biology Lab of University of Life Sciences	Tartu	Estonia
61	Bayerische Landesamt fur Walt und F	Freising	Germany
62	US EPA Western Ecology Div	Corvallis	USA
63	IRSA - CNR	Brugherio	Italy
64	S.C. ANALIST Service S.R.L.	Bucharest	Romania
65	C.N.R. Istituto Studio Ecosistemi	Pallanza	Italy
66	Soil Science and Plant Nutrition Department	Firenze	Italy
67	Lab di Microanalysis	Sesto	Italy
68	T.G. Masaryk Water Research Institute	Praha 6	Czech Republic
69	Laboratoire d,Hydrobiologie et de Geochimie	Strasbourg	France
70	Norwegian Institute for Water Research	Oslo	Norway
71	CEH Wallinford	Wallingford	United Kingdom
72	Yantai Emvironmental Monitoring Centre	Yantai	China
73	SLU – Department of Aquatic Sciences and Ass.	Uppsala	Sweden
74	Amt der Kärntner Landesregierung	Klagenfurt	Austria
75	Hydrobiological Institute, ASCR	Budejovice	Czech Republic

Number of participating laboratories from the different countries being represented in intercomparison 1024

Country	Labs	Country	Labs	Country	Labs
Austria	1	Ireland	1	Russia	7
Belgium	1	Italy	4	Scotland	1
Canada	3	Japan	2	Slovenia	3
China	1	Latvia	1	Spain	1
Czech Republic	3	Lithuania	1	Sweden	4
Estonia	4	Norway	2	Switzerland	1
Finland	5	Poland	4	United Kingdom	3
France	2	Romania	1	USA	2
Germany	5				
				Number of countries	25

Appendix B.

Preparation of samples

The sample solutions were prepared from water collected from two locations outside Oslo, Norway, two rivers called Kvisla and Langlielva. The water was collected in several 25 liter plastic containers and brought to the laboratory. The water was filtrated through 0,45 µm membrane filter, and the filtrate collected in polyethylene containers, and then stored at room temperature for several weeks at the laboratory to equilibrate. Small aliquots were removed from the filtrate to determine the background concentrations of the analytical variables of interest. The samples were prepared by spiking the filtrated water with stock solutions of stoichiometric compounds containing the major ions, or heavy metals. The samples C and D were prepared for the determination of metals, and preserved by addition of 5 ml concentrated nitric acid pr. liter sample. A few days before mailing the samples to the participants, the solutions were transferred to 1/2 liter high density polyethylene bottles with screw cap. These samples were stored at room temperature until mailing to the participating laboratories.

Sample control analyses

During the intercomparison period, four sets of samples were randomly selected from the batch for control analyses. The determinations were carried out by the laboratory at the Programme Centre, the first sample set being analyzed in June 2009, a few weeks before mailing the samples to the participants. The last sample was analyzed medio August 2009. A summary of the control results is presented in Table 3. The control results confirmed that the stability of the sample solutions were acceptable during the intercalibration period for all analytical variables except for nitrate which proved not to be stable enough.

Table 3. Summary of the control analyses

Analytical variable	Sample A		Sample B	
	Mean	Std. dev.	Mean	Std. dev.
pH	6,53	0,03	6,76	0,06
Conductivity mS/m	2,96	0,05	4,56	0,05
Alkalinity mmol/l	0,125	0,005	0,216	0,004
Nitrate-nitrogen µg/l	56	42,8	41	6,0
Chloride mg/l	1,41	0,06	4,24	0,09
Sulphate mg/l	1,15	0,05	2,23	0,07
Calcium mg/l	1,86	0,02	4,86	0,02
Magnesium mg/l	0,40	0,01	0,44	0,01
Sodium mg/l	4,14	0,03	3,34	0,03
Potassium mg/l	0,38	0,01	0,22	0,01
Total organic carbon, mg/l	20,7	0,46	5,1	0,14
	Sample C		**Sample D**	
Aluminium, µg/l	358,5	6,8	137,5	2,4
Iron, µg/l	514	10	68,8	1,5
Manganese, µg/l	20,3	0,48	16,6	0,28
Cadmium, µg/l	3,98	0,07	5,76	0,05
Lead, µg/l	4,39	0,07	6,46	0,03
Copper, µg/l	1,02	0,10	5,71	0,09
Nickel, µg/l	4,50	0,19	5,55	0,06
Zinc, µg/l	25,6	0,2	29,9	0,3

Appendix C.

Treatment of analytical data

The intercomparison was carried out by the method of Youden. This procedure requires two samples to be analyzed, and every laboratory shall report only one result for each sample and analytical variable. In a coordinate system the result of sample B is plotted against the result of sample A (see Figures 1 - 19).

The graphical presentation creates a possibility to distinguish between random and systematic errors affecting the results. The two straight lines drawn in the diagram are representing the true values of the samples; or - as in this case, when the true value is not known - the median value of the results from the participating laboratories. The results being omitted in the statistical calculations are not used in the determination of the median value and thus the true value. The diagram is thus divided into four quadrants. In a hypothetical case, when the analysis is affected by random errors only, the results will spread randomly over the four quadrants.

However, the results are usually located in the lower left and the upper right quadrant, constituting a characteristic elliptical pattern along the 45 ° line. This is reflecting the fact that many laboratories - due to systematic deviations - have attained too low or too high values for both samples.

The acceptance limit of the results may be represented by a circle with its centrum at the intersection of the two straight lines in the diagram (true or median values). The distance between the centrum of the circle, and the mark representing the laboratory, is a measure of the total error of the results. The distance along the 45 ° line is giving the magnitude of the systematic error, while the distance perpendicular to the 45 ° line is indicating the magnitude of the random error. The location of the laboratory in the diagram is an important information about the size and type of analytical error, making it easier to disclose the source of error.

The statistical treatment of the analytical results was accomplished in this way: Pairs of results where one or both of the values are lying outside the true value ± 50 %, are omitted from the statistical calculations. The remaining results are used for the calculation of the mean value (x) and the standard deviation (s). Now the pairs of results where both of the values are lying outside $x \pm 3s$, are omitted. The remaining results are used for a final calculation, the results of which are presented in the tables 5.1 - 5.19. Results being omitted from the calculations, are marked with the letter "U".

Estimation of uncertainty for the true values

The median value of the reported results, after exclusion of strongly deviating results, is used as the true value for this intercomparison. Therefore the estimation of the uncertainty of the true value is based on the method given in ISO 13528 (2005), Annex C (first part). For each

Parameter	Sample	Median	s	Cv (%)	2×s	N	U
pH	A	6,36	0,178		0,36	60	0
	B	6,57	0,208		0,42	60	0
Cond	A	2,94	0,089	3,0	0,18	58	3
	B	4,60	0,163	3,5	0,33	58	3
Alk	A	0,124	0,0193	15,6	0,0386	42	2
	B	0,220	0,0148	6,7	0,0296	42	2
NO3+NO2	A	86	11,3	13,1	22,6	53	4
	B	46	6,87	14,9	13,74	53	4
Cl	A	1,40	0,104	7,4	0,208	54	3
	B	4,27	0,171	4,0	0,342	56	1
SO4	A	1,21	0,119	9,8	0,238	54	1
	B	2,29	0,156	6,8	0,312	54	1
Ca	A	1,76	0,156	8,9	0,312	54	0
	B	4,72	0,274	5,8	0,548	54	0
Mg	A	0,386	0,0237	6,1	0,0474	53	2
	B	0,423	0,0208	4,9	0,0416	53	2
Na	A	4,17	0,171	4,1	0,342	56	0
	B	3,37	0,137	4,1	0,274	56	0
K	A	0,380	0,030	7,9	0,06	55	1
	B	0,225	0,0202	9,0	0,0404	54	2
TOC	A	18,9	1,85	9,8	3,7	33	2
	B	5,17	0,756	14,6	1,512	35	0
Al	C	379	18,7	4,9	37,4	27	3
	D	141	13,3	9,4	26,6	29	1
Fe	C	525	23,7	4,5	47,4	37	3
	D	73	5,56	7,6	11,12	35	5
Mn	C	20,5	1,19	5,8	2,38	39	1
	D	16,8	0,742	4,4	1,484	39	1
Cd	C	4,00	0,156	3,9	0,312	40	0
	D	5,77	0,274	4,7	0,548	40	0
Pb	C	4,54	0,430	9,5	0,86	38	3
	D	6,74	0,623	9,2	1,246	39	2
Cu	C	1,10	0,148	13,5	0,296	31	10
	D	5,60	0,593	10,6	1,186	39	2
Ni	C	4,52	0,371	8,2	0,742	33	5
	D	5,59	0,409	7,3	0,818	34	4
Zn	C	26,1	2,02	7,7	4,04	33	2
	D	31,5	2,22	7,0	4,44	35	0

N is the number of results used for the calculations, and U is the number of excluded results when the median value is calculated.

parameter the median value is determined, the the standard deviation for the absolute differences between the median value and the result of each participating laboratory is calculated. This value is used without further iterations to calculate the expanded uncertainty: the p results from the participants is called x_1, x_2, x_3, …. X_p, and is sorted in ascending order, strongly deviating results are already excluded. The following calculations are then performed:

m = median value of x_i (i = 1, 2 …. p)
s = 1,483 × the median of $|x_i - m|$ (i = 1, 2 …. p)

The expanded uncertainty is 2 × s, see the table onm the previous page.

Appendix D

Table 4. The results of the participating laboratories.

Lab.	pH		Conductivity, mS/m		Alkalinity, mmol/l		Nitrate-N, µg/l	
no.	A	B	A	B	A	B	A	B
1	6,16	6,41	2,95	4,73	0,08	0,22	68,4	34,2
2	5,54	6,03	3,92	3,18	0,153	0,228	84,1	43,7
3	6,45	6,64	2,85	4,48	0,145	0,230	97	47
4	6,34	6,53	2,9	4,6	0,107	0,223	85	44
5	6,54	6,91	3,05	4,75	0,128	0,215	103	60,5
6	6,47	6,84	2,85	4,54	0,065	0,109	410	406
7	6,37	6,55	2,82	4,51	0,095	0,198		
8	6,45	6,58	3,55	4,92	0,117	0,208	87	46
9	6,38	6,72	2,80	4,41			92	52
10	6,45	6,80	3,02	4,81	0,144	0,224	79	60
11	5,94	6,26	29,2	45,4			124	74,5
12	6,255	6,240	2,9	4,3	0,230	0,300	45	27
13	6,29	6,70	2,92	4,61	0,098	0,212	90	47
14	6,26	6,66	3,03	4,69			88	43
15	6,65	6,45	3,03	4,72	0,120	0,150		
16	6,75	6,90	2,98	4,65			94,1	49,5
17	6,22	6,53	2,95	4,43	0,108	0,211	20	56
18								
19	6,92	7,09	2,98	4,61			79	37
20	6,28	6,46	2,84	4,42				
21	6,52	6,75	2,96	4,54	0,13	0,21	87,5	42,8
22								
23	6,63	6,82	3,02	4,77	0,128	0,233	384	159
24								
25	6,41	6,70	2,88	4,66	0,125	0,217	93	50
26	6,32	6,47	3,013	4,75	0,131	0,226	79,1	42,9
27	6,63	7,06	2,93	4,76			98,0	50,3
28	6,27	6,43	2,68	4,40	0,125	0,206	34,0	40,0
29								
30	5,98	6,28	2,8	4,4	0,099	0,203	64	46
31								
32	6,39	6,43	3,0	4,6			81	46
33	6,66	7,03	2,9	4,6	12,500	22,500	94	52
34	6,6	6,7	2,98	4,71	0,230	0,300	138	108
35	6,37	6,72	3,1	4,7	0,157	0,257	85	40

Lab.	pH		Conductivity, mS/m		Alkalinity, mmol/l		Nitrate-N, µg/l	
no.	A	B	A	B	A	B	A	B
36			2,90	4,40	0,117	0,210	75,1	27,9
37	6,35	6,52	2,95	4,73	0,132	0,222	84,1	52,8
38	6,36	6,57	2,90	4,57	0,114	0,246	59	30
39	6,4	6,8	2,55	5,64			336	55
40	5,68	6,20	2,86	3,94	0,141	0,234	37,4	49,1
41								
42			3,03	4,64			71	45
43	6,48	6,63	3,0	4,7	0,11	0,14	93,5	46,6
44								
45	6,21	6,53	29,53	45,77			120	80
46	5,533	5,993	2,94	4,56			90	35
47	6,73	7,10	2,88	4,42			65,5	27,1
48	5,89	6,22	3,05	4,71	0,144	0,246	56,7	25,0
49	6,49	6,86	2,97	4,56	0,14	0,23	83	42
50	6,48	6,63	3,0	4,7	0,11	0,14	93,5	46,6
51	6,398	6,636	2,9	4,6	0,120	0,214	88,2	42,0
52	6,35	6,59	2,93	4,60				
53	6,34	6,47	2,920	4,605			<150	<150
54	6,31	6,65	3,00	4,70	0,125	0,214	91	52
55								
56								
57	6,32	6,55	2,93	4,61	0,12	0,22	98	47
58	6,45	6,71	3,10	4,48			85,9	45,5
59	6,20	6,43	2,95	4,67	0,136	0,221	78	45
60	6,21	6,39	3,4	5,9			82	48
61	6,70	7,07	2,66	4,30			126	87
62	6,14	6,57	30,21	44,82	0,120	0,218	81,71	43,72
63	6,39	6,60	2,73	4,42	0,125	0,230	113	75
64	5,75	6,1	3,0	5,0	0,1	0,2		
65	6,23	6,45	2,93	4,55	0,120	0,220	80	45
66	5,93	6,38	3,02	4,69			90,42	49,73
67								
68	6,16	6,28	3,01	4,58	0,21	0,305	16,4	60,2
69	6,33	6,55	3,02	4,76	0,124	0,229	111,4	73,5
70	6,55	6,85	2,90	4,49	0,119	0,210	90	50
71	6,34	6,50					90	68
72								
73	6,38	6,51	2,88	4,52	0,0983	0,2145	85	39
74								
75	6,57	6,99	2,9	4,6	0,123	0,221	90	43

Lab.	Chloride, mg/l		Sulfate, mg/l		Calcium, mg/l		Magnesium, mg/l	
no.	A	B	A	B	A	B	A	B
1	1,20	3,79	0,85	1,58	1,64	4,52	0,36	0,45
2	2,13	4,24	1,13	2,28	1,78	4,72	0,375	0,423
3	1,40	4,36	1,21	2,36	1,76	4,92	0,44	0,50
4	1,380	4,265	0,407	0,779				
5	1,3	4,4	1,2	2,3				
6	1,32	4,25	1,21	2,28	1,78	4,99	0,38	0,42
7	1,63	4,37	1,31	2,38	1,98	4,80	0,414	0,486
8	1,35	4,13	1,25	2,27	1,91	5,44	0,412	0,443
9	1,32	4,16	1,27	2,31	1,40	4,19	0,35	0,42
10	1,88	4,22	1,00	2,90	0,897	3,043	0,485	0,593
11	1,62	4,38	1,77	2,97	<1	2,86	<0,5	0,50
12	1,3216	4,1359	1,0765	2,1202	1,5096	4,4604	0,31565	0,39455
13	1,37	4,30	1,23	2,31	1,82	4,87	0,400	0,440
14	1,43	4,30	1,11	2,62	2,03	5,13	0,420	0,450
15	0,8	3,3			2,0	4,0	0,6	0,9
16	1,42	4,28	1,19	2,23				
17	1,41	4,40	0,84	2,03	1,76	4,54	0,38	0,41
18								
19	1,14	3,58	0,70	1,36	2,02	7,86	0,45	0,56
20					1,91	4,80	0,41	0,42
21	1,35	4,29	1,13	2,16	1,42	4,32	0,35	0,47
22								
23	1,38	4,41	1,11	2,14	1,80	4,81	0,40	0,45
24								
25	1,217	4,177	1,063	2,216				
26					1,80	4,84	0,40	0,45
27	1,42	4,28	1,20	2,27	1,76	4,67	0,40	0,44
28	1,50	4,40	1,25	2,35	1,64	4,48	0,380	0,415
29					1,69	4,50	0,396	0,426
30	1,45	4,51	1,32	2,42	1,67	4,38	0,38	0,42
31								
32								
33	1,39	4,23	1,27	2,42	1,70	5,09	0,41	0,44
34	2,0	4,0	1,5	2,2				
35	1,33	4,03	1,12	2,14	1,79	5,70	0,37	0,41
36	1,43	4,17	1,24	2,29	1,68	4,59	0,356	0,423
37	1,32	4,06	1,12	2,15	1,86	4,75	0,39	0,44
38	1,14	2,54	1,08	2,20	1,41	3,94	0,23	0,29
39	1,28	3,88	1,14	2,19	1,94	5,36	0,424	0,483
40	1,90	4,28	1,675	2,566	1,746	4,767	0,383	0,418

Lab.	Chloride, mg/l		Sulfate, mg/l		Calcium, mg/l		Magnesium, mg/l	
no.	A	B	A	B	A	B	A	B
41								
42					1,67	4,46	0,394	0,439
43	2,80	4,20	1,69	2,48	1,77	4,55	0,395	0,419
44								
45	1,60	5,17	1,32	3,03	1,49	4,24	0,33	0,41
46	1,424	4,349	1,219	2,308	2,457	6,002	0,492	0,498
47	1,09	3,75	0,78	1,43	1,82	4,67	0,44	0,48
48	1,42	4,06	1,24	2,48	0,17	4,51	0,39	0,44
49	1,50	1,29	4,81	2,43	1,7	5,1	0,38	0,53
50	2,8	4,2	1,69	2,48	1,77	4,55	0,395	0,419
51	1,435	5,005	1,249	2,305	1,78	4,82	0,364	0,412
52								
53	1,38	4,12	1,409	2,062	1,805	4,617	0,375	0,404
54	1,46	4,55	1,17	2,40	1,64	4,51	0,37	0,42
55								
56								
57	1,51	4,72	1,24	2,83	2,01	5,48	0,41	0,42
58	1,40	4,33	1,29	2,32	1,77	4,88	0,383	0,426
59	1,46	4,34	0,874	1,97	1,59	4,79	0,379	0,409
60								
61	1,38	4,13	1,28	2,35	1,88	4,87	0,386	0,422
62	1,374	4,185	1,134	2,204	1,797	4,863	0,385	0,432
63	1,33	4,01	1,40	2,39	1,38	3,92	0,28	0,41
64	1,65	4,6	2,0	3,06	1,36	2,73	0,80	1,27
65	1,40	4,24	1,16	2,18	1,47	4,85	0,43	0,42
66	1,46	4,30	1,20	2,30	1,98	5,00	0,42	0,45
67								
68	2,21	3,89	1,15	2,13	1,53	4,36	0,377	0,423
69	1,37	4,25	1,20	2,20	1,72	4,72	0,389	0,437
70	1,32	4,12	1,10	2,13	1,87	4,85	0,39	0,44
71	1,5	4,1	1,3	2,4	1,55	4,14	0,36	0,41
72								
73	1,44	4,28	1,25	2,30	1,74	4,71	0,36	0,41
74								
75	1,41	4,14	1,19	2,26	1,70	4,65	0,38	0,42

Lab.	Sodium, mg/l		Potassium, mg/l		TOC, mg/l		Aluminium, µg/l	
no.	A	B	A	B	A	B	C	D
1	3,65	3,07	0,38	0,23			364,6	140,4
2	4,54	3,51	1,18	0,11	16,82	4,31	295	111
3	4,32	3,52	0,43	0,26	17,3	5,09	379	140
4	4,367	3,488	0,390	0,225				
5							319,1	102,5
6	4,17	3,30	0,32	0,17	18,9	4,8	383	154
7	4,43	3,56	0,360	0,246	21,0	5,95		
8	4,35	3,20	0,18	-0,50	17,0	4,31		
9	4,12	3,29	0,38	0,23	3,87	5,24		
10	4,65	3,85	0,340	0,220				
11	4,04	3,39	<0,5	<0,5				
12	4,2437	3,4552	0,3587	0,2223			376	140
13	4,20	3,86	0,395	0,242	18,83	4,71		
14	4,21	3,39	0,380	0,230				
15	3,76	2,97	0,42	0,25				
16					19,9	5,78		
17	4,07	3,37	0,55	0,32			307	125
18								
19	3,61	2,85	0,42	0,26				
20	3,90	3,11	0,32	0,16				
21	4,16	3,32	0,38	0,27	17,9	5,36		
22								
23	4,22	3,36	0,400	0,240			405	157
24								
25					20,64	7,624		
26	4,43	3,56	0,40	0,23			402	150
27	4,15	3,28	0,38	0,22	17,4	5,17	384	145
28	4,06	3,30	0,390	0,235				
29	4,09	3,38	0,360	0,210			398	150
30	4,17	3,42	0,40	0,25			400	170
31								
32								
33	4,38	3,41	0,40	0,26	19,128	5,484		
34					19,3	6,1		
35	3,96	3,10	0,38	0,20				
36	4,38	3,45	0,375	0,221			381	138
37	4,11	3,31	0,36	0,19	20,2	5,85		
38	3,73	2,90	0,35	0,19				
39	4,61	3,78	0,397	0,246				
40	3,917	3,162	0,383	0,246	19,44	5,08	397,2	149,1

Lab.	Sodium, mg/l		Potassium, mg/l		TOC, mg/l		Aluminium, µg/l	
no.	A	B	A	B	A	B	C	D
41								
42	3,81	3,09	0,414	0,239	20,69	5,75	380	124
43	4,22	3,30	0,393	0,230	17,19	4,38	378	141
44								
45	4,15	3,37	0,39	0,22			368	133
46	4,225	3,383	0,385	0,228				
47	4,07	3,43	0,39	0,28	20,66	5,64		
48	4,27	3,51	0,47	0,55				
49	4,8	3,8	0,36	0,21	14,36	4,67		
50	4,22	3,30	0,393	0,230	17,19	4,38	378	141
51	4,646	3,634	0,358	0,206	19,05	5,16		
52								
53	4,069	3,190	0,390	0,216	24,633	11,000	366,6	143,3
54	4,01	3,24	0,36	0,22	18,3	4,73	469	129
55								
56								
57	4,15	3,31	0,34	0,19	19,4	5,23	0	153
58	4,31	3,46	0,362	0,218				
59	3,97	3,15	0,379	0,220	20,4	5,9	388	167
60					16,6	4,4		
61	4,31	3,43	0,404	0,236	20,0	5,59	373	142
62	4,227	3,382	0,400	0,245	19,09	4,82	391,6	146,2
63	4,06	3,37	0,38	0,22				
64	2,16	3,6	0,25	0,22			238	168
65	4,19	3,35	0,36	0,21	18,5	5,0	375	137
66	4,26	3,40	0,38	0,22				
67								
68	4,2	3,35	0,393	0,234	17,8	5,38	358	132
69	4,18	3,38	0,36	0,22	17,8	4,7	400	150
70	4,11	3,30	0,37	0,22	20,0	7,2	357	137
71	3,64	2,80	0,32	0,19		5,28		
72								
73	4,00	3,15	0,35	0,23	20,1	5,5	80	354
74								
75	4,12	3,27	0,38	0,22	17,2	5,3		

Lab.	Iron, µg/l		Manganese, µg/l		Cadmium, µg/l		Lead, µg/l	
no.	C	D	C	D	C	D	C	D
1	502,5	71,3	19,9	16,4	4,03	5,89	4,30	6,18
2	474	65	18,9	15,5	3,7	5,4	4,6	6,8
3	496	65	20	15	3,92	5,58	5	7
4								
5	451,8	75,09	18,43	15,08	3,91	5,58	4,14	6,03
6	548	79	20	17	4	6	5	7
7								
8								
9					4,10	6,14	4,44	6,66
10								
11			21,4	17,2	4,06	5,73	4,84	6,90
12	510	65,1	21,6	17,6	4,14	5,91	4,54	6,66
13								
14								
15			20,0	16,0	1,96	2,78	-2,00	4,8
16								
17	616	102	16,32	20,04	4,09	5,71	3,72	5,40
18								
19	543	7	18,8	18,2	5,3	8,9	4,2	8,5
20								
21			20,6	16,6	3,69	5,59	4,06	6,04
22								
23	542	76	20,9	17,3	4,07	5,90	4,77	7,03
24								
25								
26	540	72,8	21,0	17,2	4,25	6,09	4,90	7,06
27	537	73	21	17	4,13	5,80	4,58	7,12
28								
29	569	77	21,0	17,0	3,90	5,70	4,43	6,58
30	560	78	20,0	16,6	3,97	5,77	4,68	6,74
31								
32								
33	2020	2050	1970	2020				
34								
35								
36	514	71,5	21,7	17,1	3,79	5,23	5,13	7,16
37								
38								
39	470	68	20,8	17,4	4,96	6,87	4,98	7,26
40	542	75,2	20,89	16,89	3,667	5,314	4,970	8,488

Lab.	Iron, µg/l		Manganese, µg/l		Cadmium, µg/l		Lead, µg/l	
no.	C	D	C	D	C	D	C	D
41								
42	527	67	21,7	17,5	3,9	5,7	<15	<15
43	525	73,1	20,5	16,7	4,10	5,95	4,86	7,20
44								
45	496	84,5	20,1	16,6	3,88	5,60	4,40	6,50
46	523,6	73,71	19,58	16,94	4,265	6,210	4,588	6,789
47	560	70						
48								
49			20,43	16,31	3,92	5,52	4,69	7,13
50	525	73	20,5	16,7	4,10	5,95	4,86	7,20
51								
52								
53	548,78	101,21	18,44	15,84	3,9	5,5	<10	<10
54	322	26,7	20,0	14,2	3,77	5,07	2,61	3,32
55								
56								
57	511	68,5	14,6	16,0	3,2	7,1	4,4	6,7
58	504	79,0	19,5	16,1	3,94	5,73	4,35	6,37
59	529	72,2	20,2	16,5	4,03	5,76	4,53	6,69
60								
61	493	73	20,0	16,2	4,2	6,1	4,9	7,1
62	537,5	72,7	21,0	17,2	4,1	5,6	7,4	8,6
63					3,74	5,10	7,22	3,80
64	612	68,4	16,7	11,3	3,48	5,82	4,82	6,26
65	542	71	16,4	12,9	3,2	4,4	3,8	5,4
66								
67								
68	520	79,4	21,3	16,6			4,04	6,46
69	530	80	22	17	4,0	5,8	4,4	6,2
70	523	70	20,7	16,9	4,04	5,82	4,34	6,44
71								
72	523	55,1	21,3	16,9	4,12	5,94	3,71	5,69
73	39	470	10,0	19,0	4,11	5,89	4,5	6,8
74								
75								

Lab.	Copper, µg/l		Nickel, µg/l		Zinc, µg/l	
no.	C	D	C	D	C	D
1	1,16	5,83	4,71	5,82	28,1	34,1
2	1,0	5,3	4,3	5,3	24,6	28,9
3	<10	<10	<10	<10	26	28
4						
5	0,81	5,09	4,18	5,24	25,13	29,53
6	<5	6			28	32
7						
8						
9	1,09	5,60	4,60	5,60	26,6	32,1
10						
11	1,85	6,24	6,24	6,52		
12	1,12	5,66	4,69	5,50	26,9	31,4
13						
14						
15	2,6	7,4	<5	<5	22,0	32,0
16						
17	0,84	4,90	3,70	4,77	20,52	25,03
18						
19	1,2	4,1			24,8	28,9
20						
21	0,99	4,82	4,30	5,22		
22						
23	1,02	5,40	4,74	5,80	24,1	27,6
24						
25						
26	1,22	6,07	4,93	5,99	27,9	32,3
27	1,38	6,58	5,18	5,94	26	32
28						
29	1,01	5,90	4,52	5,50	21,4	22,5
30	1,0	5,5	4,60	5,80	22	23
31						
32						
33						
34						
35						
36	-2,00	4,87	5,64	5,29	25,4	29,8
37						
38						
39	1,04	5,82	4,85	6,02	31,8	34,3
40	1,134	5,531	4,780	5,776	27,60	32,79

Lab.	Copper, µg/l		Nickel, µg/l		Zinc, µg/l	
no.	C	D	C	D	C	D
41						
42	<4	4,80	<10	<10	22,0	26,8
43	1,22	6,00	4,92	6,03	27,46	32,62
44						
45	1,04	5,47	4,50	5,62	25,9	30,8
46	1,162	6,345	4,410	5,852	26,53	32,95
47						
48						
49	<1	5,48	3,72	4,76	26,00	30,65
50	1,22	6,00	4,92	6,03	27,46	32,62
51						
52						
53	<10	<10	15,0	14,0	25	31
54	1,10	5,55	4,52	5,59	30,51	34,52
55						
56						
57	<0,2	4,1	3,4	5,4	24,8	33,1
58	1,12	5,60	4,48	5,49	26,2	31,3
59	-1,00	5,38	4,33	5,44	25,7	29,8
60						
61	0,79	5,3	4,6	5,6	28,3	32,7
62	1,7	6,0	<20	<20	26,6	31,6
63	<1	3,96				
64	8,39	9,29	8,85	6,23	29,6	22,8
65	1,2	4,8	3,6	4,3	27,5	32,4
66						
67						
68	<2	5,37	4,15	4,04	30,7	34,8
69	1,20	6,10	4,7	5,9	32	39
70	0,993	5,68	4,62	5,55	25,4	30,0
71						
72	0,81	5,60	4,42	5,40	25,5	30,1
73	1,1	5,9	4,5	5,8	27	33
74						
75						

Table 5.1. Statistics - pH
Sample A

Number of participants	61	Range	1,39
Number of omitted results	0	Variance	0,07
True value	6,36	Standard deviation	0,27
Mean value	6,33	Relative standard deviation	4,3%
Median value	6,36	Relative error	-0,5%

Analytical results in ascending order:

46	5,53	54	6,31	10	6,45
2	5,54	26	6,32	8	6,45
40	5,68	57	6,32	6	6,47
64	5,75	69	6,33	50	6,48
48	5,89	53	6,34	43	6,48
66	5,93	71	6,34	49	6,49
11	5,94	4	6,34	21	6,52
30	5,98	37	6,35	5	6,54
62	6,14	52	6,35	70	6,55
1	6,16	38	6,36	75	6,57
68	6,16	35	6,37	34	6,60
59	6,20	7	6,37	27	6,63
60	6,21	73	6,38	23	6,63
45	6,21	9	6,38	15	6,65
17	6,22	63	6,39	33	6,66
65	6,23	32	6,39	61	6,70
12	6,26	51	6,40	47	6,73
14	6,26	39	6,40	16	6,75
28	6,27	25	6,41	19	6,92
20	6,28	58	6,45		
13	6,29	3	6,45		

Sample B

Number of participants	61	Range	1,11
Number of omitted results	0	Variance	0,07
True value	6,57	Standard deviation	0,26
Mean value	6,59	Relative standard deviation	3,9%
Median value	6,57	Relative error	0,3%

Analytical results in ascending order:

46	5,99	73	6,51	13	6,70
2	6,03	37	6,52	58	6,71
64	6,10	4	6,53	35	6,72
40	6,20	45	6,53	9	6,72
48	6,22	17	6,53	21	6,75
12	6,24	57	6,55	10	6,80
11	6,26	69	6,55	39	6,80
30	6,28	7	6,55	23	6,82
68	6,28	62	6,57	6	6,84
66	6,38	38	6,57	70	6,85
60	6,39	8	6,58	49	6,86
1	6,41	52	6,59	16	6,90
32	6,43	63	6,60	5	6,91
59	6,43	43	6,63	75	6,99
28	6,43	50	6,63	33	7,03
65	6,45	51	6,64	27	7,06
15	6,45	3	6,64	61	7,07
20	6,46	54	6,65	19	7,09
26	6,47	14	6,66	47	7,10
53	6,47	25	6,70		
71	6,50	34	6,70		

U = Omitted result

Table 5.2. Statistics - Conductivity, mS/m
Sample A

Number of participants	62	Range	0,44
Number of omitted results	7	Variance	0,01
True value	2,94	Standard deviation	0,09
Mean value	2,93	Relative standard deviation	3,1%
Median value	2,94	Relative error	-0,2%

Analytical results in ascending order:

39	2,55	U	12	2,90		32	3,00	
61	2,66		13	2,92		68	3,01	
28	2,68		53	2,92		26	3,01	
63	2,73		27	2,93		66	3,02	
30	2,80		65	2,93		69	3,02	
9	2,80		52	2,93		10	3,02	
7	2,82		57	2,93		23	3,02	
20	2,84		46	2,94		42	3,03	
3	2,85		1	2,95		14	3,03	
6	2,85		37	2,95		15	3,03	
40	2,86		17	2,95		5	3,05	
47	2,88		59	2,95		48	3,05	
25	2,88		21	2,96		58	3,10	
73	2,88		49	2,97		35	3,10	
4	2,90		34	2,98		60	3,40	U
51	2,90		19	2,98		8	3,55	U
33	2,90		16	2,98		2	3,92	U
38	2,90		64	3,00		11	29,20	U
70	2,90		43	3,00		45	29,53	U
75	2,90		50	3,00		62	30,21	U
36	2,90		54	3,00				

Sample B

Number of participants	62	Range	1,06
Number of omitted results	7	Variance	0,03
True value	4,60	Standard deviation	0,16
Mean value	4,59	Relative standard deviation	3,5%
Median value	4,60	Relative error	-0,3%

Analytical results in ascending order:

2	3,18	U	49	4,56		43	4,70	
40	3,94		38	4,57		35	4,70	
12	4,30		68	4,58		48	4,71	
61	4,30		51	4,60		34	4,71	
30	4,40		52	4,60		15	4,72	
36	4,40		4	4,60		37	4,73	
28	4,40		75	4,60		1	4,73	
9	4,41		33	4,60		26	4,75	
63	4,42		32	4,60		5	4,75	
47	4,42		53	4,61		27	4,76	
20	4,42		19	4,61		69	4,76	
17	4,43		13	4,61		23	4,77	
58	4,48		57	4,61		10	4,81	
3	4,48		42	4,64		8	4,92	U
70	4,49		16	4,65		64	5,00	
7	4,51		25	4,66		39	5,64	U
73	4,52		59	4,67		60	5,90	U
21	4,54		66	4,69		62	44,82	U
6	4,54		14	4,69		11	45,40	U
65	4,55		54	4,70		45	45,77	U
46	4,56		50	4,70				

U = Omitted result

Table 5.3. Statistics - Alkalinity, mmol/l

Sample A

Number of participants	43	Range	0,077
Number of omitted results	7	Variance	0,000
True value	0,124	Standard deviation	0,017
Mean value	0,122	Relative standard deviation	13,9%
Median value	0,124	Relative error	-1,2%

Analytical results in ascending order:

6	0,065	U	57	0,120		37	0,132	
1	0,080		62	0,120		59	0,136	
7	0,095		65	0,120		49	0,140	
13	0,098		51	0,120		40	0,141	
73	0,098		15	0,120		10	0,144	
30	0,099		75	0,123		48	0,144	
64	0,100		69	0,124		3	0,145	
4	0,107		54	0,125		2	0,153	
17	0,108		28	0,125		35	0,157	
50	0,110	U	25	0,125		68	0,210	U
43	0,110	U	63	0,125		34	0,230	U
38	0,114		23	0,128		12	0,230	U
8	0,117		5	0,128		33	12,500	U
36	0,117		21	0,130				
70	0,119		26	0,131				

Sample B

Number of participants	43	Range	0,107
Number of omitted results	7	Variance	0,000
True value	0,220	Standard deviation	0,017
Mean value	0,219	Relative standard deviation	7,9%
Median value	0,220	Relative error	-0,6%

Analytical results in ascending order:

6	0,109	U	54	0,214		69	0,229	
50	0,140	U	73	0,215		49	0,230	
43	0,140	U	5	0,215		3	0,230	
15	0,150		25	0,217		63	0,230	
7	0,198		62	0,218		23	0,233	
64	0,200		65	0,220		40	0,234	
30	0,203		1	0,220		38	0,246	
28	0,206		57	0,220		48	0,246	
8	0,208		75	0,221		35	0,257	
21	0,210		59	0,221		12	0,300	U
70	0,210		37	0,222		34	0,300	U
36	0,210		4	0,223		68	0,305	U
17	0,211		10	0,224		33	22,500	U
13	0,212		26	0,226				
51	0,214		2	0,228				

U = Omitted result

Table 5.4. Statistics - Nitrate + nitrite-nitrogen, µg/l

Sample A

Number of participants	58	Range	46
Number of omitted results	15	Variance	108
True value	86	Standard deviation	10
Mean value	84	Relative standard deviation	12,3%
Median value	86	Relative error	-1,8%

Analytical results in ascending order:

53	< 150	U	60	82		25	93				
68	16	U	49	83		43	93				
17	20	U	2	84		50	93				
28	34	U	37	84		33	94				
40	37	U	73	85		16	94				
12	45	U	4	85		3	97				
48	57		35	85		57	98				
38	59		58	86		27	98				
30	64		8	87		5	103				
47	66		21	88		69	111	U			
1	68		14	88		63	113	U			
42	71		51	88		45	120	U			
36	75		71	90		11	124	U			
59	78		75	90		61	126	U			
19	79		46	90		34	138	U			
10	79		13	90		39	336	U			
26	79		70	90		23	384	U			
65	80		66	90		6	410	U			
32	81		54	91							
62	82		9	92							

Sample B

Number of participants	58	Range	43
Number of omitted results	15	Variance	71
True value	46	Standard deviation	8
Mean value	45	Relative standard deviation	18,7%
Median value	46	Relative error	-2,4%

Analytical results in ascending order:

53	< 150	U	4	44		33	52				
48	25		59	45		9	52				
12	27	U	42	45		54	52				
47	27		65	45		37	53				
36	28		58	46		39	55	U			
38	30		32	46		17	56	U			
1	34		30	46		10	60				
46	35		8	46		68	60	U			
19	37		50	47		5	61				
73	39		43	47		71	68				
35	40		3	47		69	74	U			
28	40	U	13	47		11	75	U			
51	42		57	47		63	75	U			
49	42		60	48		45	80	U			
21	43		40	49	U	61	87	U			
26	43		16	50		34	108	U			
14	43		66	50		23	159	U			
75	43		25	50		6	406	U			
2	44		70	50							
62	44		27	50							

U = Omitted result

Table 5.5. Statistics - Chloride, mg/l

Sample A

Number of participants	57	Range	0,81
Number of omitted results	8	Variance	0,02
True value	1,40	Standard deviation	0,15
Mean value	1,41	Relative standard deviation	10,4%
Median value	1,40	Relative error	1,0%

Analytical results in ascending order:

15	0,80	U	62	1,37		30	1,45	
47	1,09		61	1,38		66	1,46	
19	1,14		53	1,38		54	1,46	
38	1,14	U	23	1,38		59	1,46	
1	1,20		4	1,38		28	1,50	
25	1,22		33	1,39		49	1,50	U
39	1,28		58	1,40		71	1,50	
5	1,30		65	1,40		57	1,51	
37	1,32		3	1,40		45	1,60	
9	1,32		17	1,41		11	1,62	
6	1,32		75	1,41		7	1,63	
70	1,32		48	1,42		64	1,65	
12	1,32		16	1,42		10	1,88	
35	1,33		27	1,42		40	1,90	
63	1,33		46	1,42		34	2,00	U
21	1,35		36	1,43		2	2,13	U
8	1,35		14	1,43		68	2,21	U
13	1,37		51	1,44		43	2,80	U
69	1,37		73	1,44		50	2,80	U

Sample B

Number of participants	57	Range	1,59
Number of omitted results	8	Variance	0,07
True value	4,27	Standard deviation	0,27
Mean value	4,26	Relative standard deviation	6,3%
Median value	4,27	Relative error	-0,2%

Analytical results in ascending order:

49	1,29	U	75	4,14		14	4,30	
38	2,54	U	9	4,16		13	4,30	
15	3,30	U	36	4,17		66	4,30	
19	3,58		25	4,18		58	4,33	
47	3,75		62	4,19		59	4,34	
1	3,79		43	4,20	U	46	4,35	
39	3,88		50	4,20	U	3	4,36	
68	3,89	U	10	4,22		7	4,37	
34	4,00	U	33	4,23		11	4,38	
63	4,01		65	4,24		5	4,40	
35	4,03		2	4,24	U	17	4,40	
48	4,06		69	4,25		28	4,40	
37	4,06		6	4,25		23	4,41	
71	4,10		4	4,27		30	4,51	
53	4,12		27	4,28		54	4,55	
70	4,12		40	4,28		64	4,60	
61	4,13		16	4,28		57	4,72	
8	4,13		73	4,28		51	5,01	
12	4,14		21	4,29		45	5,17	

U = Omitted result

Table 5.6. Statistics - Sulfate, mg/l

Sample A

Number of participants	56	Range	0,99
Number of omitted results	4	Variance	0,04
True value	1,21	Standard deviation	0,20
Mean value	1,22	Relative standard deviation	16,1%
Median value	1,21	Relative error	0,8%

Analytical results in ascending order:

4	0,41	U	68	1,15	73	1,25
19	0,70	U	65	1,16	33	1,27
47	0,78		54	1,17	9	1,27
17	0,84		16	1,19	61	1,28
1	0,85		75	1,19	58	1,29
59	0,87		66	1,20	71	1,30
10	1,00		27	1,20	7	1,31
25	1,06		5	1,20	30	1,32
12	1,08		69	1,20	45	1,32
38	1,08		6	1,21	63	1,40
70	1,10		3	1,21	53	1,41
14	1,11		46	1,22	34	1,50
23	1,11		13	1,23	40	1,68
37	1,12		36	1,24	50	1,69
35	1,12		48	1,24	43	1,69
2	1,13		57	1,24	11	1,77
21	1,13		51	1,25	64	2,00
62	1,13		8	1,25	49	4,81
39	1,14		28	1,25		

Sample B

Number of participants	56	Range	1,60
Number of omitted results	4	Variance	0,07
True value	2,30	Standard deviation	0,27
Mean value	2,30	Relative standard deviation	11,8%
Median value	2,30	Relative error	0,4%

Analytical results in ascending order:

4	0,78	U	62	2,20	3	2,36
19	1,36	U	25	2,22	7	2,38
47	1,43		16	2,23	63	2,39
1	1,58		75	2,26	71	2,40
59	1,97		8	2,27	54	2,40
17	2,03		27	2,27	33	2,42
53	2,06		6	2,28	30	2,42
12	2,12		2	2,28	49	2,43
68	2,13		36	2,29	43	2,48
70	2,13		66	2,30	48	2,48
35	2,14		5	2,30	50	2,48
23	2,14		73	2,30	40	2,57
37	2,15		51	2,31	14	2,62
21	2,16		46	2,31	57	2,83
65	2,18		13	2,31	10	2,90
39	2,19		9	2,31	11	2,97
38	2,20		58	2,32	45	3,03
69	2,20		28	2,35	64	3,06
34	2,20		61	2,35		

U = Omitted result

Table 5.7. Statistics - Calcium, mg/l

Sample A

Number of participants	56	Range	0,65
Number of omitted results	6	Variance	0,03
True value	1,76	Standard deviation	0,16
Mean value	1,73	Relative standard deviation	9,5%
Median value	1,76	Relative error	-1,6%

Analytical results in ascending order:

11	< 1	U	36	1,68		23	1,80	
48	0,17	U	29	1,69		26	1,80	
10	0,90	U	75	1,70		53	1,81	
64	1,36	U	33	1,70		13	1,82	
63	1,38		49	1,70		47	1,82	
9	1,40		69	1,72		37	1,86	
38	1,41		73	1,74		70	1,87	
21	1,42		40	1,75		61	1,88	
65	1,47		17	1,76		8	1,91	
45	1,49		3	1,76		20	1,91	
12	1,51		27	1,76		39	1,94	
68	1,53		58	1,77		7	1,98	
71	1,55		50	1,77		66	1,98	
59	1,59		43	1,77		15	2,00	
54	1,64		6	1,78		57	2,01	
1	1,64		51	1,78		19	2,02	U
28	1,64		2	1,78		14	2,03	
30	1,67		35	1,79		46	2,46	U
42	1,67		62	1,80				

Sample B

Number of participants	56	Range	1,78
Number of omitted results	6	Variance	0,14
True value	4,72	Standard deviation	0,37
Mean value	4,70	Relative standard deviation	7,9%
Median value	4,72	Relative error	-0,3%

Analytical results in ascending order:

64	2,73	U	17	4,54		65	4,85	
11	2,86	U	50	4,55		70	4,85	
10	3,04	U	43	4,55		62	4,86	
63	3,92		36	4,59		61	4,87	
38	3,94		53	4,62		13	4,87	
15	4,00		75	4,65		58	4,88	
71	4,14		27	4,67		3	4,92	
9	4,19		47	4,67		6	4,99	
45	4,24		73	4,71		66	5,00	
21	4,32		69	4,72		33	5,09	
68	4,36		2	4,72		49	5,10	
30	4,38		37	4,75		14	5,13	
42	4,46		40	4,77		39	5,36	
12	4,46		59	4,79		8	5,44	
28	4,48		7	4,80		57	5,48	
29	4,50		20	4,80		35	5,70	
54	4,51		23	4,81		46	6,00	U
48	4,51	U	51	4,82		19	7,86	U
1	4,52		26	4,84				

U = Omitted result

Table 5.8. Statistics - Magnesium, mg/l

Sample A

Number of participants	56	Range	0,212
Number of omitted results	5	Variance	0,001
True value	0,386	Standard deviation	0,034
Mean value	0,388	Relative standard deviation	8,7%
Median value	0,386	Relative error	0,6%

Analytical results in ascending order:

11	< 0,5	U	28	0,380		27	0,400	
38	0,230	U	6	0,380		23	0,400	
63	0,280		17	0,380		57	0,410	
12	0,316		49	0,380		20	0,410	
45	0,330		75	0,380		33	0,410	
9	0,350		58	0,383		8	0,412	
21	0,350		40	0,383		7	0,414	
36	0,356		62	0,385		66	0,420	
73	0,360		61	0,386		14	0,420	
71	0,360		69	0,389		39	0,424	
1	0,360		37	0,390		65	0,430	
51	0,364		70	0,390		3	0,440	
54	0,370		48	0,390		47	0,440	
35	0,370		42	0,394		19	0,450	
2	0,375		50	0,395		10	0,485	U
53	0,375		43	0,395		46	0,492	
68	0,377		29	0,396		15	0,600	U
59	0,379		26	0,400		64	0,800	U
30	0,380		13	0,400				

Sample B

Number of participants	56	Range	0,165
Number of omitted results	5	Variance	0,001
True value	0,423	Standard deviation	0,033
Mean value	0,437	Relative standard deviation	7,5%
Median value	0,423	Relative error	3,4%

Analytical results in ascending order:

38	0,290	U	6	0,420		8	0,443	
12	0,395		54	0,420		26	0,450	
53	0,404		20	0,420		1	0,450	
59	0,409		75	0,420		14	0,450	
63	0,410		61	0,422		23	0,450	
73	0,410		68	0,423		66	0,450	
71	0,410		2	0,423		21	0,470	
35	0,410		36	0,423		47	0,480	
45	0,410		29	0,426		39	0,483	
17	0,410		58	0,426		7	0,486	
51	0,412		62	0,432		46	0,498	
28	0,415		69	0,437		3	0,500	
40	0,418		42	0,439		11	0,500	U
50	0,419		37	0,440		49	0,530	
43	0,419		70	0,440		19	0,560	
57	0,420		13	0,440		10	0,593	U
30	0,420		33	0,440		15	0,900	U
65	0,420		48	0,440		64	1,270	U
9	0,420		27	0,440				

U = Omitted result

Table 5.9. Statistics - Sodium, mg/l

Sample A

Number of participants	57	Range	1,19
Number of omitted results	1	Variance	0,06
True value	4,17	Standard deviation	0,25
Mean value	4,16	Relative standard deviation	5,9%
Median value	4,17	Relative error	-0,1%

Analytical results in ascending order:

64	2,16	U	29	4,09		46	4,23	
19	3,61		70	4,11		62	4,23	
71	3,64		37	4,11		12	4,24	
1	3,65		75	4,12		66	4,26	
38	3,73		9	4,12		48	4,27	
15	3,76		27	4,15		58	4,31	
42	3,81		57	4,15		61	4,31	
20	3,90		45	4,15		3	4,32	
40	3,92		21	4,16		8	4,35	
35	3,96		30	4,17		4	4,37	
59	3,97		6	4,17		36	4,38	
73	4,00		69	4,18		33	4,38	
54	4,01		65	4,19		7	4,43	
11	4,04		13	4,20		26	4,43	
28	4,06		68	4,20		2	4,54	
63	4,06		14	4,21		39	4,61	
53	4,07		50	4,22		51	4,65	
17	4,07		43	4,22		10	4,65	
47	4,07		23	4,22		49	4,80	

Sample B

Number of participants	57	Range	1,06
Number of omitted results	1	Variance	0,05
True value	3,37	Standard deviation	0,22
Mean value	3,34	Relative standard deviation	6,5%
Median value	3,37	Relative error	-0,8%

Analytical results in ascending order:

71	2,80		43	3,30		33	3,41	
19	2,85		70	3,30		30	3,42	
38	2,90		28	3,30		47	3,43	
15	2,97		57	3,31		61	3,43	
1	3,07		37	3,31		36	3,45	
42	3,09		21	3,32		12	3,46	
35	3,10		68	3,35		58	3,46	
20	3,11		65	3,35		4	3,49	
73	3,15		23	3,36		48	3,51	
59	3,15		63	3,37		2	3,51	
40	3,16		17	3,37		3	3,52	
53	3,19		45	3,37		7	3,56	
8	3,20		29	3,38		26	3,56	
54	3,24		69	3,38		64	3,60	U
75	3,27		62	3,38		51	3,63	
27	3,28		46	3,38		39	3,78	
9	3,29		11	3,39		49	3,80	
50	3,30		14	3,39		10	3,85	
6	3,30		66	3,40		13	3,86	

U = Omitted result

Table 5.10. Statistics - Potassium, mg/l

Sample A

Number of participants	57	Range	0,110
Number of omitted results	6	Variance	0,001
True value	0,380	Standard deviation	0,025
Mean value	0,378	Relative standard deviation	6,6%
Median value	0,380	Relative error	-0,6%

Analytical results in ascending order:

11	< 0,5	U	58	0,362		4	0,390	
8	0,180	U	70	0,370		50	0,393	
64	0,250	U	36	0,375		43	0,393	
6	0,320		59	0,379		68	0,393	
71	0,320		63	0,380		13	0,395	
20	0,320		9	0,380		39	0,397	
10	0,340		27	0,380		30	0,400	
57	0,340		14	0,380		33	0,400	
73	0,350		1	0,380		23	0,400	
38	0,350		66	0,380		62	0,400	
51	0,358		21	0,380		26	0,400	
12	0,359		35	0,380		61	0,404	
54	0,360		75	0,380		42	0,414	
29	0,360		40	0,383		19	0,420	
7	0,360		46	0,385		15	0,420	
49	0,360		28	0,390		3	0,430	
69	0,360		53	0,390		48	0,470	U
37	0,360		45	0,390		17	0,550	U
65	0,360		47	0,390		2	1,180	U

Sample B

Number of participants	57	Range	0,120
Number of omitted results	6	Variance	0,001
True value	0,225	Standard deviation	0,023
Mean value	0,226	Relative standard deviation	10,3%
Median value	0,225	Relative error	0,3%

Analytical results in ascending order:

11	< 0,5	U	59	0,220		68	0,234	
8	< 0,5	U	54	0,220		28	0,235	
2	0,110	U	69	0,220		61	0,236	
20	0,160		10	0,220		42	0,239	
6	0,170		45	0,220		23	0,240	
71	0,190		75	0,220		13	0,242	
38	0,190		70	0,220		62	0,245	
37	0,190		64	0,220	U	40	0,246	
57	0,190		36	0,221		7	0,246	
35	0,200		12	0,222		39	0,246	
51	0,206		4	0,225		30	0,250	
49	0,210		46	0,228		15	0,250	
65	0,210		14	0,230		3	0,260	
29	0,210		73	0,230		33	0,260	
53	0,216		9	0,230		19	0,260	
58	0,218		1	0,230		21	0,270	
63	0,220		50	0,230		47	0,280	
66	0,220		26	0,230		17	0,320	U
27	0,220		43	0,230		48	0,550	U

U = Omitted result

Table 5.11. Statistics - Total organic carbon, mg/l

Sample A

Number of participants	35	Range	6,64	
Number of omitted results	4	Variance	2,31	
True value	18,90	Standard deviation	1,52	
Mean value	18,63	Relative standard deviation	8,2%	
Median value	18,90	Relative error	-1,4%	

Analytical results in ascending order:

71		U	69	17,80		16	19,90	
9	3,87	U	21	17,90		70	20,00	
49	14,36		54	18,30		61	20,00	
60	16,60		65	18,50		73	20,10	
2	16,82		13	18,83		37	20,20	
8	17,00		6	18,90		59	20,40	
43	17,19		51	19,05		25	20,64	U
50	17,19		62	19,09		47	20,66	
75	17,20		33	19,13		42	20,69	
3	17,30		34	19,30		7	21,00	
27	17,40		57	19,40		53	24,63	U
68	17,80		40	19,44				

Sample B

Number of participants	35	Range	2,89	
Number of omitted results	4	Variance	0,41	
True value	5,17	Standard deviation	0,64	
Mean value	5,22	Relative standard deviation	12,3%	
Median value	5,17	Relative error	0,9%	

Analytical results in ascending order:

2	4,31		40	5,08		61	5,59	
8	4,31		3	5,09		47	5,64	
43	4,38		51	5,16		42	5,75	
50	4,38		27	5,17		16	5,78	
60	4,40		57	5,23		37	5,85	
49	4,67		9	5,24	U	59	5,90	
69	4,70		71	5,28	U	7	5,95	
13	4,71		75	5,30		34	6,10	
54	4,73		21	5,36		70	7,20	
6	4,80		68	5,38		25	7,62	U
62	4,82		33	5,48		53	11,00	U
65	5,00		73	5,50				

U = Omitted result

Table 5.12. Statistics - Aluminium, µg/l

Sample C

Number of participants			
Number of omitted results	30	Range	174
True value	3	Variance	1090
Mean value	379	Standard deviation	33
Median value	377	Relative standard deviation	8,8%
	379	Relative error	-0,6%

Analytical results in ascending order:

57	0	U	45	368		27	384	
73	80	U	61	373		59	388	
64	238	U	65	375		62	392	
2	295		12	376		40	397	
17	307		50	378		29	398	
5	319		43	378		30	400	
70	357		3	379		69	400	
68	358		42	380		26	402	
1	365		36	381		23	405	
53	367		6	383		54	469	

Sample D

Number of participants			
Number of omitted results	30	Range	68
True value	3	Variance	214
Mean value	141	Standard deviation	15
Median value	141	Relative standard deviation	10,4%
	141	Relative error	-0,3%

Analytical results in ascending order:

5	103		3	140		69	150	
2	111		12	140		29	150	
42	124		1	140		26	150	
17	125		50	141		57	153	U
54	129		43	141		6	154	
68	132		61	142		23	157	
45	133		53	143		59	167	
65	137		27	145		64	168	U
70	137		62	146		30	170	
36	138		40	149		73	354	U

U = Omitted result

Table 5.13. Statistics - Iron, µg/l

Sample C

Number of participants			
Number of omitted results	37	Range	160
True value	6	Variance	970
Mean value	525	Standard deviation	31
Median value	524	Relative standard deviation	5,9%
	525	Relative error	-0,2%

Analytical results in ascending order:

73	39	U	68	520		23	542	
54	322	U	72	523		65	542	
5	452		70	523		19	543	U
39	470		46	524		6	548	
2	474		50	525		53	549	U
61	493		43	525		30	560	
45	496		42	527		47	560	
3	496		59	529		29	569	
1	503		69	530		64	612	
58	504		27	537		17	616	U
12	510		62	538		33	2020	U
57	511		26	540				
36	514		40	542				

Sample D

Number of participants			
Number of omitted results	37	Range	29
True value	6	Variance	33
Mean value	73	Standard deviation	6
Median value	72	Relative standard deviation	7,9%
	73	Relative error	-0,9%

Analytical results in ascending order:

19	7	U	1	71		29	77	
54	27	U	36	72		30	78	
72	55		59	72		58	79	
3	65		62	73		6	79	
2	65		26	73		68	79	
12	65		61	73		69	80	
42	67		27	73		45	85	
39	68		50	73		53	101	U
64	68		43	73		17	102	U
57	69		46	74		73	470	U
70	70		5	75		33	2050	U
47	70		40	75				
65	71		23	76				

U = Omitted resultat

Table 5.14. Statistics - Manganese, µg/l

Sample C

Number of participants			
Number of omitted results	40	Range	5,7
True value	4	Variance	1,7
Mean value	20,5	Standard deviation	1,3
Median value	20,2	Relative standard deviation	6,4%
	20,5	Relative error	-1,5%

Analytical results in ascending order:

73	10,0	U	30	20,0		27	21,0	
57	14,6	U	6	20,0		62	21,0	
17	16,3		15	20,0		26	21,0	
65	16,4		3	20,0		29	21,0	
64	16,7	U	45	20,1		72	21,3	
5	18,4		59	20,2		68	21,3	
53	18,4		49	20,4		11	21,4	
19	18,8		50	20,5		12	21,6	
2	18,9		43	20,5		36	21,7	
58	19,5		21	20,6		42	21,7	
46	19,6		70	20,7		69	22,0	
1	19,9		39	20,8		33	1970,0	U
54	20,0		40	20,9				
61	20,0		23	20,9				

Sample D

Number of participants			
Number of omitted results	40	Range	7,1
True value	4	Variance	1,3
Mean value	16,8	Standard deviation	1,2
Median value	16,6	Relative standard deviation	6,9%
	16,8	Relative error	-1,1%

Analytical results in ascending order:

64	11,3	U	68	16,6		36	17,1	
65	12,9		30	16,6		11	17,2	
54	14,2		21	16,6		26	17,2	
3	15,0		45	16,6		62	17,2	
5	15,1		43	16,7		23	17,3	
2	15,5		50	16,7		39	17,4	
53	15,8		40	16,9		42	17,5	
15	16,0		72	16,9		12	17,6	
57	16,0	U	70	16,9		19	18,2	
58	16,1		46	16,9		73	19,0	U
61	16,2		27	17,0		17	20,0	
49	16,3		6	17,0		33	2020,0	U
1	16,4		29	17,0				
59	16,5		69	17,0				

U = Omitted resultat

Table 5.15. Statistics - Cadmium, µg/l

Sample C

Number of participants			
Number of omitted results	40	Range	1,07
True value	4	Variance	0,05
Mean value	4,00	Standard deviation	0,22
Median value	3,95	Relative standard deviation	5,5%
	4,00	Relative error	-1,2%

Analytical results in ascending order:

15	1,96	U	5	3,91		9	4,10	
65	3,20	U	49	3,92		43	4,10	
57	3,20		3	3,92		62	4,10	
64	3,48		58	3,94		73	4,11	
40	3,67		30	3,97		72	4,12	
21	3,69		6	4,00		27	4,13	
2	3,70		69	4,00		12	4,14	
63	3,74		59	4,03		61	4,20	
54	3,77		1	4,03		26	4,25	
36	3,79		70	4,04		46	4,27	
45	3,88		11	4,06		39	4,96	U
42	3,90		23	4,07		19	5,30	U
53	3,90		17	4,09				
29	3,90		50	4,10				

Sample D

Number of participants			
Number of omitted results	40	Range	2,03
True value	4	Variance	0,13
Mean value	5,77	Standard deviation	0,36
Median value	5,76	Relative standard deviation	6,2%
	5,77	Relative error	-0,1%

Analytical results in ascending order:

15	2,78	U	42	5,70		12	5,91	
65	4,40	U	29	5,70		72	5,94	
54	5,07		17	5,71		43	5,95	
63	5,10		58	5,73		50	5,95	
36	5,23		11	5,73		6	6,00	
40	5,31		59	5,76		26	6,09	
2	5,40		30	5,77		61	6,10	
53	5,50		69	5,80		9	6,14	
49	5,52		27	5,80		46	6,21	
3	5,58		70	5,82		39	6,87	U
5	5,58		64	5,82		57	7,10	
21	5,59		73	5,89		19	8,90	U
62	5,60		1	5,89				
45	5,60		23	5,90				

U = Omitted resultat

Table 5.16. Statistics - Lead, µg/l

Sample C

Number of participants			
Number of omitted results	41	Range	1,42
True value	6	Variance	0,14
Mean value	4,54	Standard deviation	0,37
Median value	4,53	Relative standard deviation	8,3%
	4,54	Relative error	-0,3%

Analytical results in ascending order:

42	< 15	U	57	4,40		64	4,82	
53	< 10	U	45	4,40		11	4,84	
15	< 2	U	69	4,40		50	4,86	
54	2,61	U	29	4,43		43	4,86	
72	3,71		9	4,44		61	4,90	
17	3,72		73	4,50		26	4,90	
65	3,80		59	4,53		40	4,97	
68	4,04		12	4,54		39	4,98	
21	4,06		27	4,58		3	5,00	
5	4,14		46	4,59		6	5,00	
19	4,20		2	4,60		36	5,13	
1	4,30		30	4,68		63	7,22	U
70	4,34		49	4,69		62	7,40	U
58	4,35		23	4,77				

Sample D

Number of participants			
Number of omitted results	41	Range	3,10
True value	6	Variance	0,43
Mean value	6,74	Standard deviation	0,66
Median value	6,73	Relative standard deviation	9,8%
	6,74	Relative error	-0,2%

Analytical results in ascending order:

42	< 15	U	70	6,44		6	7,00	
53	< 10	U	68	6,46		23	7,03	
54	3,32	U	45	6,50		26	7,06	
63	3,80	U	29	6,58		61	7,10	
15	4,80	U	9	6,66		27	7,12	
17	5,40		12	6,66		49	7,13	
65	5,40		59	6,69		36	7,16	
72	5,69		57	6,70		43	7,20	
5	6,03		30	6,74		50	7,20	
21	6,04		46	6,79		39	7,26	
1	6,18		73	6,80		40	8,49	
69	6,20		2	6,80		19	8,50	
64	6,26		11	6,90		62	8,60	U
58	6,37		3	7,00				

U = Omitted resultat

Table 5.17. Statistics - Copper, µg/l

Sample C

Number of participants			
Number of omitted results	41	Range	0,59
True value	14	Variance	0,02
Mean value	1,10	Standard deviation	0,14
Median value	1,07	Relative standard deviation	13,4%
	1,10	Relative error	-2,5%

Analytical results in ascending order:

53	< 10	U	21	0,99		1	1,16	
3	< 10	U	70	0,99		46	1,16	
6	< 5	U	30	1,00		69	1,20	
42	< 4	U	2	1,00		19	1,20	
36	< 2	U	29	1,01		65	1,20	
68	< 2	U	23	1,02		43	1,22	
63	< 1	U	45	1,04		50	1,22	
59	< 1	U	39	1,04		26	1,22	
49	< 1	U	9	1,09		27	1,38	
57	< 0,2	U	73	1,10		62	1,70	U
61	0,79		54	1,10		11	1,85	U
5	0,81		12	1,12		15	2,60	U
72	0,81		58	1,12		64	8,39	U
17	0,84		40	1,13				

Sample D

Number of participants			
Number of omitted results	41	Range	2,48
True value	14	Variance	0,27
Mean value	5,60	Standard deviation	0,52
Median value	5,57	Relative standard deviation	9,4%
	5,60	Relative error	-0,5%

Analytical results in ascending order:

53	< 10	U	59	5,38	U	73	5,90	
3	< 10	U	23	5,40		29	5,90	
63	3,96	U	45	5,47		62	6,00	U
19	4,10		49	5,48	U	50	6,00	
57	4,10	U	30	5,50		6	6,00	U
65	4,80		40	5,53		43	6,00	
42	4,80	U	54	5,55		26	6,07	
21	4,82		58	5,60		69	6,10	
36	4,87	U	9	5,60		11	6,24	U
17	4,90		72	5,60		46	6,35	
5	5,09		12	5,66		27	6,58	
2	5,30		70	5,68		15	7,40	U
61	5,30		39	5,82		64	9,29	U
68	5,37	U	1	5,83				

U = Omitted resultat

Table 5.18. Statistics - Nickel, µg/l

Sample C

Number of participants			
Number of omitted results	38	Range	2,24
True value	7	Variance	0,21
Mean value	4,52	Standard deviation	0,46
Median value	4,50	Relative standard deviation	10,2%
	4,52	Relative error	-0,4%

Analytical results in ascending order:

62	< 20	U	46	4,41		1	4,71	
42	< 10	U	72	4,42		23	4,74	
3	< 10	U	58	4,48		40	4,78	
15	< 5	U	73	4,50		39	4,85	
57	3,40		45	4,50		43	4,92	
65	3,60		54	4,52		50	4,92	
17	3,70		29	4,52		26	4,93	
49	3,72		30	4,60		27	5,18	
68	4,15		61	4,60		36	5,64	
5	4,18		9	4,60		11	6,24	U
21	4,30		70	4,62		64	8,85	U
2	4,30		12	4,69		53	15,00	U
59	4,33		69	4,70				

Sample D

Number of participants			
Number of omitted results	38	Range	1,99
True value	7	Variance	0,23
Mean value	5,59	Standard deviation	0,48
Median value	5,50	Relative standard deviation	8,8%
	5,59	Relative error	-1,7%

Analytical results in ascending order:

62	< 20	U	72	5,40		73	5,80	
42	< 10	U	59	5,44		1	5,82	
3	< 10	U	58	5,49		46	5,85	
15	< 5	U	29	5,50		69	5,90	
68	4,04		12	5,50		27	5,94	
65	4,30		70	5,55		26	5,99	
49	4,76		54	5,59		39	6,02	
17	4,77		61	5,60		43	6,03	
21	5,22		9	5,60		50	6,03	
5	5,24		45	5,62		64	6,23	U
36	5,29		40	5,78		11	6,52	U
2	5,30		23	5,80		53	14,00	U
57	5,40		30	5,80				

U = Omitted resultat

Table 5.19. Statistics - Zinc, µg/l

Sample C

Number of participants			
Number of omitted results	38	Range	11,5
True value	0	Variance	7,1
Mean value	26,1	Standard deviation	2,7
Median value	26,3	Relative standard deviation	10,1%
	26,1	Relative error	0,7%

Analytical results in ascending order:

17	20,5	72	25,5	50	27,5
29	21,4	59	25,7	65	27,5
15	22,0	45	25,9	40	27,6
30	22,0	3	26,0	26	27,9
42	22,0	49	26,0	6	28,0
23	24,1	27	26,0	1	28,1
2	24,6	58	26,2	61	28,3
19	24,8	46	26,5	64	29,6
57	24,8	9	26,6	54	30,5
53	25,0	62	26,6	68	30,7
5	25,1	12	26,9	39	31,8
70	25,4	73	27,0	69	32,0
36	25,4	43	27,5		

Sample D

Number of participants			
Number of omitted results	38	Range	16,5
True value	0	Variance	11,7
Mean value	31,5	Standard deviation	3,4
Median value	30,8	Relative standard deviation	11,1%
	31,5	Relative error	-2,4%

Analytical results in ascending order:

29	22,5	72	30,1	50	32,6
64	22,8	49	30,7	43	32,6
30	23,0	45	30,8	61	32,7
17	25,0	53	31,0	40	32,8
42	26,8	58	31,3	46	33,0
23	27,6	12	31,4	73	33,0
3	28,0	62	31,6	57	33,1
19	28,9	15	32,0	1	34,1
2	28,9	27	32,0	39	34,3
5	29,5	6	32,0	54	34,5
59	29,8	9	32,1	68	34,8
36	29,8	26	32,3	69	39,0
70	30,0	65	32,4		

U = Omitted resultat

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